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Handbook for Pesticide Disposal by Common Chemical Methods

TRW Systems Group

Prepared For
Environmental Protection Agency

December 1975

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HANDBOOK FOR PESTICIDE DISPOSAL

BY COMMON CHEMICAL METHODS

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The recommended detoxification procedures contained in this report are based on information that is believed to be reliable and best efforts have been made to confirm the information obtained. However, no warranty or guarantee is made concerning the accuracy or sufficiency of any information, and TRW does not assume any responsibility in connection with any accidents or injuries which may result from using the detoxification procedures prescribed in this report.

ACKNOWLEDGEMENT

This project is deeply indebted to the EPA Project Officer, Mr. Harry W. Trask, for his continuing advice and guidance during the course of the study. Thanks are also due to other staff members of the Office of Solid Waste Management Programs for their critical review of the draft final report.

ABSTRACT

The present study is concerned with examining the practicability of utilizing chemical degradation/detoxification methods for the disposal of small quantities of pesticide wastes. The objectives of the study are twofold: (i) to develop procedures to advise pesticide users of safe and readily available chemical methods for pesticide disposal; and (ii) to delineate the hazards associated with pesticide disposal by common chemical methods. A total of twenty pesticides representative of the major pesticide classes were investigated. Based on a review of the literature on pesticide chemistry and information provided by the pesticide manufacturers, it was determined that treatment with alkali is an effective and environmentally safe method for the disposal of small quantities of naled, diazinon, Guthion, malathion, carbaryl, captan, and atrazine. For these seven pesticides, detailed disposal procedures were developed to give directions on the quantities and concentrations of caustic soda and additives to be used, the contact time required to complete the degradation process, and the methods for handling reaction product mixtures and rinse solutions. The review and analysis of the information collected also indicate no practical chemical degradation/detoxification methods exist for the disposal of Dursban, methyl parathion, maneb, alachlor (Lasso), diuron, picloram, trifluralin, methoxychlor, chlordane, toxaphene, 2,4-D, amiben (chloramben), and pentachlorophenol.

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SUMMARY

This study is concerned with examining the practicability of utilizing chemical degradation/detoxification methods for the disposal of small quantities of pesticides wastes. A primary objective of the study is to develop procedures to advise pesticide users of safe, readily available chemical methods for pesticide disposal. A second objective, of equal importance, is to delineate the hazards associated with pesticide disposal by chemical methods, and to warn the laymen against the indiscriminate use of chemical disposal methods based on incomplete knowledge of the degradation products or the hazardous nature of the detoxifying reagents.

The approach was to conduct an in-depth investigation on twenty key pesticides representative of each major pesticide class, rather than attempt to cover all commercially available pesticides. The pesticides were classified into chemical families. The principal criteria used in selecting the representative pesticides from each chemical class were production volume and toxicity. Secondary considerations in the selection of the pesticides included the representativeness of the chemical structure of the pesticide within the chemical class, persistence in the soil, mobility, and solubility in water. The twenty pesticides selected for the TRW study were:

- Phosphorus-containing pesticides - naled, diazinon, Dursban (chlorpyrifos), methyl parathion, Guthion (azinphosmethyl), and malathion.
- Nitrogen-containing pesticides - carbaryl (Sevin), maneb, alachlor (Lasso), captan, diuron, atrazine, picloram, and trifluralin.
- Chlorine-containing pesticides - methoxychlor, chlordane, toxaphene, 2,4-D, amiben (chloramben), and pentachlorophenol.

Identification of practical chemical degradation/detoxification methods for pesticide disposal was accomplished by a review of the literature on pesticide chemistry. In addition, the manufacturers were directly contacted for readily available information and published instructions. The emphasis was on simple chemical disposal methods suitable for use by laymen.

From the results of the review, it was determined that treatment with alkali is an effective and environmentally safe method for the disposal of small quantities of naled, diazinon, Guthion, malathion, carbaryl, captan and atrazine. This conclusion was reached after careful assessment of the completeness of the degradation process and the identity and toxicity of the degradation products. The disposal procedures presented in this report give directions on the quantities and concentrations of caustic soda and additives to be used, The contact time required to complete the degradation process, and methods for handling reaction product mixtures and rinse solutions

Equally important, the review and analysis of the information collected also indicate no practical chemical degradation/detoxification methods exist for the disposal of Dursban, methyl parathion, maneb, alachlor (Lasso), diuron, picloram, trifluralin, methoxychlor, chlordane, toxaphene, 2,4-D, amiben (chloramben) and pentachlorophenol. Chemical methods are not recommended for one or more of the following reasons:

- The extent of chemical degradation is unknown or incomplete.
- The identify of the degradation products are unknown.
- The environmental hazards of the degradation products are unknown.
- The chemical reagents involved are expensive and hazardous.
- The chemical degradation products are hazardous.

Of particular concern is the hazardous nature of the pesticide degradation products not often recognized by laymen. For example, the degradation products from the acid or alkaline hydrolysis of methyl parathion, maneb, alachlor, and diuron are either toxic or may lead to the formation of suspected carcinogens.

Overall, chemical detoxification can be an effective method for the disposal of small quantities of certain pesticide wastes. At the same time, it should be noted that the applicability of a chemical treatment method to pesticide disposal must be evaluated in terms of each specific pesticide. The reaction chemistry between the pesticide requiring disposal and the chemical decontaminant used, as well as the environmental

hazards of the degradation products, must be sufficiently understood before a chemical detoxification procedure is employed. The final recommendations on the twenty pesticides investigated are summarized in Table 1.

TABLE 1

CHEMICAL DISPOSAL OF PESTICIDES

Do	Don't
Use alkali:	Use chemical treatment:
Naled	Dursban
Diazinon	Methyl Parathion
Guthion	Maneb
Malathion	Alachlor (Lasso)
Carbaryl	Diuron
Captan	Picloram
Atrazine	Trifluralin
Precautions:	Methoxychlor
Use personal protection equipment. Follow disposal procedure closely. Dispose larger quantities in several smaller batches.	Chlordane
	Toxaphene
	2,4-D
	Amiben
	Pentachlorophenol

1. INTRODUCTION

The improper disposal of surplus pesticides and used pesticide containers is a problem that poses a threat to both man and the environment. The normal recommended disposal methods, principally incineration or burial in specially designated landfills, have not been practiced by a majority of the end users of pesticides due to the scarcity of available facilities. For a number of pesticides, chemical degradation/detoxification offers the best alternative as an environmentally acceptable method for the disposal of small quantities of pesticides. Like incineration, the degradation products of the chemical treatment of pesticides can be predicated and controlled by the selection of appropriate chemical reagents and reaction conditions. The adequacy of a chemical treatment method can be determined from the knowledge of the extent of degradation, and the identity and environmental hazards of the degradation products.

The present study is aimed at the gathering of information necessary for the development of procedures to advise pesticide users of safe, readily available chemical methods for pesticide disposal. Another purpose is to provide pesticide users with a tool that will permit them to evaluate the feasibility of utilizing chemical degradation procedures contained in labels or labeling of pesticide products. Equally important, this study will warn the laymen of the hazards associated with the chemical degradation of many pesticides, including the hazardous nature of the end products as well as the operating hazards. To accomplish these objectives, the TRW program was organized into the following project elements:

a. Selection of 20 representative pesticides;

b. Identification of practical chemical degradation/detoxification methods for pesticide disposal;

c. Development of pesticide disposal procedures.

The 20 pesticides investigated were selected to represent each major pesticide class from the multiplicity of pesticidal compounds which cover a wide range of chemical structures. The principal criteria used in

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selecting the representative pesticides from each chemical class were the production volume and toxicity, and a prioritization model was utilized to quantify the combined effects of these two factors. Secondary considerations in the selection of the pesticides included the representativeness of the chemical structure of the pesticide within the chemical class, persistence in the soil, mobility, and solubility in water. The 20 pesticides selected for the TRW study were:

- Phosphorus-containing pesticides - naled, diazinon, Dursban (chlorpyrifos), methyl parathion, Guthion (azinphosmethyl), and malathion.
- Nitrogen-containing pesticides - carbaryl (Sevin), maneb, alachlor (Lasso), captan, diuron, atrazine, picloram, and trifluralin.
- Chlorine-containing pesticides - methoxychlor, chlordane, toxaphene, 2,4-D, amiben (chloramben), and pentachlorophenol.

The identification of practical chemical degradation/detoxification methods for pesticide disposal was accomplished by an extensive review of the literature on pesticide chemistry. In addition, the manufacturers of the selected pesticides were directly contacted for readily available information and published instructions on methods of chemical detoxification. The emphasis was on simple chemical disposal methods suitable for use by laymen, such as alkaline hydrolysis and chemical oxidation by sodium hypochlorite treatment. Equal importance was also placed on the identification of pesticides that should not be treated by the common chemical methods, as a result of incomplete knowledge of the degradation products or the generation of degradation products that were equally or more toxic than the starting material.

The information collected on the most practical and reliable methods for the chemical degradation/detoxification of the selected pesticides was utilized to develop disposal procedures which give directions on the quantities and concentrations of the reagents and additives to be used, as well as the handling of the reaction product mixtures and rinse solutions. The

final recommended procedures are based on the recommendations of the pesticide manufacturers and the National Agricultural Chemicals Association together with information from the literature, taking into account the considerations that the detoxifying reagents used should be relatively common and low in cost, easy to handle, and pose no significant hazard to man and the environment. For the pesticides for which chemical degradation/detoxification techniques were not applicable, alternate methods for the disposal of small quantities of these pesticides have been suggested. The incorporation of the input from the pesticide manufacturers into the final recommendations, as well as the approach to concentrate on a selected number of key pesticides, are the major differences between the present TRW study and similar types of studies on the chemical degradation of pesticides.

The main body of this report is divided into four sections, the first of which is this introduction. Section 2 describes the selection of the representative pesticides for this study. In Section 3, the recommended procedures for the disposal of small quantities of pesticides and the decontamination of pesticide containers are presented. The conclusions and recommendations that have resulted from the TRW investigation are summarized in Section 4. The detailed review and discussion of the chemical methods available for the degradation/detoxification of the phosphorus, nitrogen, and chlorine containing pesticides are presented in Appendices A, B and C, respectively. The triple rinse and drain procedure for pesticide containers developed by the National Agricultural Chemicals Association is included in Appendix D of this report.

2. CLASSIFICATION AND SELECTION OF PESTICIDES

Over several hundred insecticides, herbicides and fungicides are presently being sold in the United States and consequently, a complete study to determine the recommended chemical degradation/detoxification methods for all or a majority of these pesticides would be a major effort and outside the scope of this program. Therefore, the approach utilized in this program was to select an appropriate number of key pesticides representative of each major pesticide class.

2.1 CLASSIFICATION OF PESTICIDES

For the present study, the classification of pesticides into chemical families of compounds is more relevant than the classification according to use patterns or applied characteristics, and the pesticide classification system suggested by the Midwest Research Institute (MRI) in the "Guidelines for the Disposal of Small Quantities of Unused Pesticides" report, with minor modifications, is most applicable.[1] The MRI system classifies the pesticides into seven major categories:

- Inorganic and metallo-organic pesticides
- Phosphorus-containing pesticides
- Nitrogen-containing pesticides
- Halogen-containing pesticides
- Sulfur-containing pesticides
- Botanical and microbiological pesticides
- Organic pesticides, not elsewhere classified

The predominant inorganic and metallo-organic pesticides are compounds containing either arsenic, mercury or copper, and the fundamental toxic character of these metals or elements cannot be destroyed by any chemical

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method. The inorganic and metallo-organic pesticides were therefore not considered in this study. The sulfur-containing pesticides do not pose serious toxicity or environmental hazards and as with the botanical and microbiological pesticides, are not produced in significant quantities. For these reasons, it is more appropriate to classify the pesticides which might utilize chemical detoxification into four major categories:

- Phosphorus-containing pesticides
- Nitrogen-containing pesticides
- Halogen-containing pesticides
- Miscellaneous pesticides

It should be noted that according to this pesticide classification system, a pesticide that contains phosphorus, nitrogen, halogen and other elements is normally classified as a phosphorus compound. The usefulness of this method of classification is supported by the fact that the decomposition chemistry of a pesticide containing phosphorus and other elements will most likely depend primarily on the chemistry of the phosphorus-containing portion of the molecule.

To ensure the proper selection of representative pesticides, the further classification of pesticides within each major category is necessary. Again, the MRI system for subclassification, with a number of modifications and combinations, is used. The revised pesticide classification system is presented in Table 2, together with examples of typical pesticides in each pesticide class.

2.2 PRIORITIZATION SYSTEM FOR PESTICIDE SELECTION

The criteria used in the selection of representative pesticides from each chemical class included: the quantity of the pesticide requiring disposal, its hazard to the environment, and the representativeness of the chemical structure of the pesticide within the chemical class. To provide for a quantitative basis of the selection process, a simple model was developed for prioritizing the pesticides within each chemical subclass. In the

TABLE 2

PESTICIDE CLASSIFICATION SYSTEM

Pesticide Class		Typical Pesticides in Each Chemical Class
I.	Phosphorus-Containing Pesticides	
(i)	Phosphates and Phosphonates	Mevinphos, TEPP, Azodrin, Dichlorvos, Bidrin, Naled
(ii)	Phosphorothioates	Diazinon, Methyl Parathion, Parathion, Demeton, Dursban, Fenthion, Zinophos, Dasanit
(iii)	Phosphorodithioates	Disulfoton, Phorate, Malathion, Guthion, Ethion, Trithion
(iv)	Other Organophosphates	Ruelene, DEF Defoliant, Folex
II.	Nitrogen-Containing Pesticides	
(i)	Carbamates, Thiocarbamates and Dithiocarbamates	Carbaryl, Aldicarb, Carbofuran, Bux Ten, Sutan, Eptam, Maneb, Ferbam, Zineb
(ii)	Amides, Anilides, Imides, and Hydrazides	Diphenamid, Alachlor, Randox, Propachlor, Captan, Difolatan, MH
(iii)	Ureas and Uracils	Diuron, Linuron, Monuron, Bromacial
(iv)	Triazines	Atrazine, Propazine, Simazine
(v)	Amines, Nitro Compounds, and Quaternary Ammonium Compounds	Picloram, Trifluralin, Benefin, Nitralin, Dinoseb, Diquat, Paraquat
(vi)	Other Nitrogen-Containing Compounds	Antu, Dodine, Naptalam
III.	Halogen-Containing Pesticides	
(i)	DDT and Related Compounds	Methoxychlor, Chlorobenzilate, Dicofol
(ii)	Chlorophenoxy Compounds	2,4-D, Silvex, 2,4,5-T, MCPA
(iii)	Aldrin-Toxaphene Group	Chlordane, Toxaphene, Endrin, Heptachlor
(iv)	Dihaloaromatic Compounds	Amiben, Paradichlorobenzene, Banvel
(v)	Highly Halogenated Compounds	Pentachlorophenol, Fenac, Dacthal
IV.	Miscellaneous Pesticides	Warfarin, Endothall, Fumarin, Rotenone, Pyrethins, Sodium Fluoroacetate, Omite

development of the priority ranking model, the pesticide waste quantity factor was considered to be of equal importance as the environmental hazard factor in establishing priorities; i.e., a highly toxic or hazardous pesticide waste generated in relatively small quantities was considered equally damaging as a moderately toxic or hazardous pesticide waste generated in relatively large quantities. The simplest mathematical relationship that expresses this type of priority ranking for hazard and quantity factors r_f and Q respectively, is the product function:

$$PR = r_f \cdot Q$$

where PR is the numerical ranking factor. Since the quantity of the pesticide requiring disposal is directly related to the production volume,* the quantity factor Q was assigned with values related to the annual production volume of each pesticide as follows:

Annual Production Volume of Pesticide	Q
>45,400 metric tons (100 million lb) per year	1000
4540 to 45,400 metric tons (10 to 100 million lb) per year	100
454 to 4540 metric tons (1 to 10 million lb) per year	10
<454 metric tons (1 million lb) per year	1

The hazard rating factor r_f was more difficult to define, since a pesticide may be classified as hazardous by virtue of any number of factors. It may present an oral, dermal, or inhalation toxicity hazard. It may be toxic to aquatic life if leachate from the soil reaches surface waters. It may be subject to bioconcentration, or represent a carcinogenic, mutagenic, or teratogenic hazard. In addition, all these hazard factors may be magnified by the persistence of the pesticide in soil, or its mobility and solubility in water.

*Except in the case of DDT, where all domestic production is for export.

In general, there will be more than one reason to rate a pesticide as hazardous. The National Academy of Sciences - National Research Council, (NAS-NRC), faced with a similar problem in evaluating potential hazards of industrial chemicals, concluded that it was only possible to rank with respect to each particular phase of the total hazard, considered by itself. It was also noted that any attempt to use mathematical operations to produce an index or composite in the form of one number should be discouraged, since such oversimplification can produce confusion and misunderstanding.

For the purposes of this program, the hazard factor, r_f, was calculated on the basis of the "worst" potential hazard presented by the pesticide. Numerical values of r_f were assigned with reference to Table 3, which was derived from the NAS-NRC Report: "System for Evaluation of the Hazards of Bulk Water Transportation of Industrial Chemicals", with the appropriate modifications.[2] The flammability and reactivity hazards have both been eliminated from the rating system, as these are not hazards generally associated with pesticides. Also, in the NAS-NRC report, four hazard "grades" are defined, ranging from slightly hazardous to extremely hazardous. In Table 2, r values of 1, 10, 100 or 1000 have been arbitrarily assigned to NAS-NRC Grades 1, 2, 3 and 4 respectively, and r_f is taken as the highest value of r exhibited by the pesticide in any hazard category. According to the proposed hazard rating system, a pesticide such as DDT which is known to bioaccumulate in the food chain, has a 48-hour TL_m of 0.0021 mg/l for fish and a moderate acute oral toxicity, is assigned the highest hazard rating of 1000 because of either its bioaccumulative property or its extreme hazard to aquatic life.

It may be noted that the hazard rating system does not include either mobility or persistence in the soil among its hazard categories. Mobility or persistence in the soil is not a hazard in itself and only serves to increase the degree of a hazard already present. The mobility of a pesticide depends on the physico-chemical properties of the pesticide as well as the soil and must take into account such factors as formulation type, solubility, ionic charge of the pesticide and the moisture content, temperature, pH and organic matter and clay contents of the soil. Mobility

TABLE 3

HAZARD RATING SYSTEM

Hazard Category	Hazard Rating (r)			
	1000	100	10	1
1. Bioaccumulation	Bioaccumulated and liable to produce a hazard to aquatic life or human health			Not known to be significantly bioaccumulated
2. Oral Toxicity	LD_{50} < 5 mg/kg	LD_{50} 5-50 mg/kg	LD_{50} 50-500 mg/kg	LD_{50} 500-5000 mg/kg
3. Inhalation Toxicity	LC_{50} ≤ 50 ppm or ≤ 0.5 mg/l or or OSHA 1 ppm	LC_{50} 50-200 ppm or 0.5-2mg/l or OSHA 1-10 ppm	LC_{50} 200-2000 ppm or OSHA 10-100 ppm	OSHA 100-1000 ppm
4. Dermal Toxicity	LD_{50} ≤ 20 mg/kg 24 hour skin contact	LD_{50} 20-200 mg/kg 24 Hour skin contact	Corrosive to skin	Lachrymators
5. Aquatic Toxicity	TL_m <1 mg/l	TL_m 1-10 mg/l	TL_m 10-100 mg/l	TL_m 100-1000 mg/l
6. Teratogenicity	Known to be teratogenic			Not known to be teratogenic
7. Carcinogenicity	Known to be carcinogenic			Not known to be carcinogenic
8. Mutagenicity	Known to be mutagenic			Not known to be mutagenic
r_f is the highest value of r exhibited by the pesticide in any hazard category.				

data, based on soil thin-layer chromatography, are only available for the most common soil-applied pesticides. The pesticide mobility factor was therefore only a secondary consideration in the selection of the candidate pesticides. The persistence of a pesticide in soil depends to a large extent on its chemical classification. For example, organochlorine insecticides are the most persistent pesticides (from 1 to 5 years), whereas the organophosphate insecticides do not persist for long periods in most soils (less than 3 months). Since the candidate pesticides were selected to represent each chemical class listed in Table 2 and pesticides of the same chemical class normally persist in soil for similar periods of time, the persistence factor was again only a secondary consideration in the selection process.

Although both Q and r_f may assume values of 1, 10, 100 or 1000, there are no pesticides produced at over 45,400 metric tons (100 million lb) per year and hence the highest Q value possible is 100 and the product PR can range from 1 to 10^5 in multiples of 10. For convenience, the discussion on the selection of the candidate pesticides will refer to log PR rather than PR. Thus a log PR rating of 5 is the highest priority ranking and a log PR rating of 1 is the lowest priority ranking in the selection process.

2.3 SELECTION OF CANDIDATE PESTICIDES

The selection of the candidate pesticides is discussed with reference to the chemical classification system presented in Table 2.

Phosphorus-Containing Pesticides

(i) Phosphates and Phosphonates. Naled was the only pesticide assigned with the top log PR rating of 4 for this group and was selected.

(ii) Phosphorothioates. This is one of the most important chemical subclass of pesticides. Two pesticides were assigned the highest possible log

PR rating of 5 in this group - diazinon and parathion. Four other pesticides in this group were assigned the high log PR rating of 4 - chloropynifos (Dursban), dasanit, methyl parathion, and ronnell. Methyl parathion was selected over parathion to represent this group because it is one of the largest volume insecticide produced and parathion is being displaced more and more by methyl parathion. In addition, diazinon and Dursban were selected.

(iii) Phosphorodithioates. Malathion was assigned the highest possible log PR rating of 5 in this group and was selected. Five other pesticides in this group were assigned the high log PR rating of 4 - azinphosmethyl (Guthion), carbophenothion (Trithion), disulfoton (Di-Syston), ethion, and phorate (Thimet). Azinphosmethyl is the only heterocyclic derivative of dithiophosphoric acid with a high log PR rating of 4 and was selected. The heterocyclic derivatives of dithiophosphoric acid have a strong insecticidal effect not only on suckling plant pests, but also on various leaf-eating insects. In many cases these compounds are very promising as substitutes for the chlorine-containing insecticides such as DDT and have attracted increasing attention.

(iv) Other Organophosphates. The only pesticide from this group assigned a log PR rating of 4 was the DEF-defoliant. The DEF defoliant is only moderately toxic to animals, and its high priority rating was due to its aquatic toxicity - a 48-hour TL_m of 0.036 mg/l for fish. Since six pesticides have already been selected to represent the three most important chemical subclass of phosphorus-containing pesticides, no pesticide from this rather inhomogeneous group was selected.

Nitrogen-Containing Pesticides

(i) Carbamates, Thiocarbamates and Dithiocarbamates. Carbaryl (Sevin) and aldicarb (Temik) were the two pesticides assigned the log PR rating of 4 for the carbamates. Carbaryl was selected over aldicarb to represent the carbamates because of its much larger production volume. In addition, the salts of substituted dithiocarbamic acids, and especially the salts of

ethylenebis (dithiocarbamic) acid, are the most widely used fungicides employed for the protection of growing plants. Maneb was selected to represent the dithiocarbamates because the production of other fungicides in this group such as nabam and zineb are gradually being reduced.

(ii) Amides, Anilides, Imides and Hydrazides. Captan was the only pesticide in this group assigned with a log PR rating of 5 and was therefore selected. Difolatan was assigned a log PR rating of 4 but belongs to the imide group already represented by the higher priority captan. Three other pesticides in this group were assigned with a log PR rating of 2 - alachlor (Lasso), CDAA (Randox), and propachlor (Ramrod). All three are volume herbicides and fungicides of moderate hazard produced at over 4,540 metric tons (10 million lb) per year. Alachlor was selected as the second representative pesticide from this group because its production volume was twice that of CDAA (9080 metric tons vs 4540 metric tons in 1972), and it has a longer residual action in soil than propachlor (ten to twelve weeks versus four to six weeks).

(iii) Ureas and Uracils. Diuron was the only pesticide from this group assigned with a log PR rating of 3 and was therefore selected. Diuron is also persistent and slightly mobile in soil.

(iv) Triazines. Atrazine, Dyrene, propazine and simazine were all assigned with a log PR rating of 3. Atrazine was selected over the three other pesticides to represent this group because it is produced in much larger quantities.

(v) Amines, Nitro Compounds, and Quaternary Ammonium Compounds. Trifluralin was assigned with the highest log PR rating of 5 because of its aquatic toxicity and large production volume. Trifluralin was selected to represent the nitro compounds. In addition, picloram, which was assigned with a log PR rating of 3, was selected to represent the amine compounds. Picloram is persistent in soil, mobile, and water-soluble, and small amounts of this herbicide irrigated on sensitive crops could lead to disastrous results.

(vi) Other Nitrogen-Containing Pesticides. There are no major pesticides included in this group and none was selected.

Halogen-Containing Pesticides

(i) DDT and Related Compounds. Methoxychlor was assigned with the log PR rating of 5 and was selected to represent this group.

(ii) Chlorophenoxy Compounds. 2,4-D was the only pesticide in this group assigned with the log PR rating of 5 and was selected.

(iii) Aldrin-Toxaphene Group. Both chlordane and toxaphene were assigned with the log PR rating of 5 and were selected.

(iv) Dihaloaromatic Compounds. Chloramben (amiben) and paradichlorobenzene were both large volume pesticides (over 9,000 metric tons per year) assigned with a log PR rating of 2. Dichlone was assigned with a higher log PR rating of 3, but its production volume is unknown and presumably much less than 454 metric tons (1 million lb) per year. Also, paradichlorobenzene is generally formulated as the 100 percent crystals, popular for domestic use against clothes moths and does not present a significant disposal problem. Chloramben was therefore selected to represent this group.

(v) Highly Halogenated Compounds. Pentachlorophenol was the only pesticide in this group assigned with a high log PR rating of 5 and was selected.

Miscellaneous Pesticides

Warfarin is the only pesticide in this group produced in significant quantities and is not suitable for disposal by chemical methods. None of the pesticides in this group can be considered as representative and none was selected.

The list of the candidate pesticides selected for the present study is presented in Table 4. In Table 5, the production volume and the hazard properties of the selected pesticides are summarized. It may be noted that the list of candidate pesticides includes all the pesticides with an annual production volume of over 4,540 metric tons (10 million lbs), with the

TABLE 4
LIST OF SELECTED PESTICIDES

Pesticide Class		Candidate Pesticides
I.	Phosphorus-Containing Pesticides	
(i)	Phosphates and Phosphonates	Naled
(ii)	Phosphorothioates	Diazinon, Methyl Parathion, Dursban
(iii)	Phosphorodithioates	Guthion, Malathion
II.	Nitrogen-Containing Pesticides	
(i)	Carbamates, Thiocarbamates, and Dithiocarbamates	Carbaryl, Maneb
(ii)	Amides, Anilides, Imides, and Hydrazides	Alachlor, Captan
(iii)	Ureas and Uracils	Diuron
(iv)	Triazines	Atrazine
(v)	Amines, Nitro Compounds, Quaternary Ammonium Compounds	Picloram, Trifluralin
III.	Halogen-Containing Pesticides	
(i)	DDT and Related Compounds	Methoxychlor
(ii)	Chlorophenoxy Compounds	2,4-D
(iii)	Aldrin-Toxaphene Group	Chlordane, Toxaphene
(iv)	Dihaloaromatic Compounds	Amiben
(v)	Highly Halogenated Compounds	Pentachlorophenol

TABLE 5

PRODUCTION VOLUME AND HAZARD PROPERTIES OF THE SELECTED PESTICIDES*

Pesticide	Production Volume (Metric Tons Per Year)	Production Rating Q	Hazards†				Hazard Rating r_f	Log (Q,r_f)	Persistence in Soil (Months)	Mobility	Water Solubility‡
			Acute Oral LD_{50} (mg/kg)	Acute Dermal LD_{50} (mg/kg)	48-hour TL_m (mg/l)	Other Hazards					
Naled	910	10	430	800	0.078	--	1,000	4	--	--	Insoluble
Diazinon	4,540	100	300-850	>2,150	0.03	--	1,000	5	3-12	Slightly mobile	40 ppm
Methyl Parathion	20,430	100	14-24	67	3	--	100	4	1-3	Slightly mobile	55 ppm
Dursban	2,270	10	135	2,000	0.02	--	1,000	4	1-3	--	2 ppm
Guthion	1,820	10	16	220	0.01	--	1,000	4	--	Slightly mobile	33 ppm
Malathion	13,620	100	2,800	4,100	0.02	--	1,000	5	1-3	--	145 ppm
Carbaryl	20,430	100	850	4,000	1.5	--	100	4	1-3	--	40 ppm at 30°C
Maneb	454-4,540	10	6,750	>1,000	1-10	--	100	3	--	--	Slightly mobile
Alachlor	9,080	100	1,200	>2,000	--	--	1	2	--	--	40 ppm
Captan	39,600	100	9,000	--	0.3	--	1,000	5	--	--	<0.5 ppm
Diuron	2,720	10	3,400	--	4.3	--	100	3	>12	Slightly mobile	42 ppm
Atrazine	40,860	100	3,080	--	12.6	--	10	3	>12	Slightly mobile	33 ppm
Picloram	1,360	10	8,200	>4,000	2.5	--	100	3	>12	Mobile	430 ppm
Trifluralin	11,350	100	10,000	>5,000	0.011	--	1,000	5	3-12	Immobile	<1 ppm
Methoxychlor	4,540	100	6,000	--	0.007	--	1,000	5	--	--	Insoluble
2,4-D	20,430	100	375-805	--	0.8-2.1	--	1,000	5	1-3	Mobile	620 ppm
Chlordane	11,350	100	457-590	690	0.01	--	1,000	5	>12	Immobile	Insoluble
Toxaphene	22,700	100	80-90	1,075	0.003	--	1,000	5	--	Immobile	Insoluble
Amiben	9,080	100	5,620	>3,160	--	--	1	2	1-3	--	700 ppm
Pentachlorophenol	20,880	10	25-200	150-350	0.2	--	1,000	5	--	--	20 ppm at 30°C

*Production volume data are 1972 figures obtained from Reference 1. The oral and dermal hazard data were obtained from References 3 and 4. The aquatic toxicity data were obtained from References 5, 6 and 7. The data on persistence in soil, mobility and water solubility were obtained from References 3, 8 and 9.

†The acute oral and dermal LD_{50} values are for rats. The 48-hour TL_m values are for fish.

‡Water solubility data are at 25°C, unless otherwise specified. Also, note that the potassium salt of picloram, the sodium salt of pentachlorophenol, and the amine salt of 2,4-D are very soluble in water.

exception of propachlor, CDAA, parathion, methyl bromide, the arsenic-containing organic pesticides and the inorganic pesticides. As discussed previously, both propachlor and CDAA are similar in chemical structure to alachlor, which has been selected, also, parathion is similar in chemical structure to the selected methyl parathion. Methyl bromide is usually stored in returnable pressurized containers and does not present a significant disposal problem. The arsenic-containing organic pesticides and the inorganic pesticides are generally not suitable for treatment by chemical degradation/detoxification methods.

3. RECOMMENDED PROCEDURE FOR THE DISPOSAL OF SELECTED PESTICIDES

The identification of practical chemical degradation/detoxification methods for pesticide disposal was accomplished by an extensive review of the literature on pesticide chemistry. In addition, the manufacturers of the selected pesticides were directly contacted for readily available information and published instructions on methods of chemical detoxification. The detailed review and discussion of the chemical methods available for the degradation/detoxification of the phosphorus, nitrogen and chlorine containing pesticides are presented in Appendices A, B, and C of this report. From the results of analysis of the information collected, it was determined that treatment with alkali is an effective and environmentally safe method for the disposal of small quantities of naled, diazinon, Guthion, malathion, carbaryl, captan, and atrazine. For the other 13 pesticides investigated, practical chemical methods for disposal are not available at the present time. In most cases, the only available practical method for the disposal of small quantities of these pesticides is either land burial or ground surface disposal, although incineration at high temperatures (above 1000 C for a minimum of 2 sec) is the preferred disposal method in all cases.

The personal protection equipment needed in the disposal of pesticides are given in Table 6. The type and quantity of decontaminant solution as well as the contact time recommended for the detoxification of the seven pesticides where chemical methods are applicable are given in Table 7. The recommended contact time is based on the calculated residence time required to cause 99.9 percent degradation of the pesticide. A minimum of 15 minutes has been allowed for the degradation reaction to complete even for reactions that are practically instantaneous. Also, in the case of wettable powder and dust formulations, a contact time of twice the nominal requirements is recommended to allow for the diffusion and absorption of the reactants into the solid particulates. In the case of diazinon, it may also be noted that alkali treatment is recommended over acid treatment as the preferred chemical disposal method. This is because acid treatment of diazinon could lead to

TABLE 6

PERSONAL PROTECTION EQUIPMENT FOR PESTICIDE DISPOSAL*

The decontaminant solution recommended for the chemical detoxification of pesticides and pesticide containers in most cases is strong caustic that can severely burn skin, eyes, or any body tissue. In addition, inhalation and skin contact with the pesticides, and especially the organophosphates, is extremely dangerous. To avoid contact with the decontaminant solution and the pesticide in the disposal of small quantities of pesticides or pesticide containers, the following protective equipment is recommended:

1. Impervious or rubber head covering.
2. Protective eye goggles.
3. Organic vapor respirators, cartridge type.
4. Washable work clothing.
5. Natural rubber gloves.
6. Latex rubber apron, ankle length.
7. Rubber work shoes or overshoes.

It should be noted that most household gloves deteriorate when handling organophosphates and therefore should not be used. Also, leather shoes should not be worn. The organic vapor respirators could be any type approved by the U.S. Department of Agriculture.

The rubber gloves, shoes, apron, and head covering may be obtained through a rubber goods house or safety equipment companies. The eye goggles, work clothing and organic vapor respirator may be obtained from safety equipment companies or sometimes through the Sears and Roebuck farm catalog.

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* References 10, 11, 12, and 13.

TABLE 7

RECOMMENDED DECONTAMINANT SOLUTION AND CONTACT TIME FOR THE CHEMICAL DETOXIFICATION OF SELECTED PESTICIDES

Pesticide	Formulation*	Decontaminant Solution	Ratio of Decontaminant Solution to Formulation	Contact Time
Naled	8 lb/gal EC	5% NaOH -	10:1 by volume	15 min
	4% D	50% ethanol	1/2 gal to 1 lb	30 min
Diazinon	60% EC	5% NaOH -	10:1 by volume	40 min
	25% EC	50% ethanol	5:1 by volume	40 min
	WP, D		1/2 gal to 1 lb	80 min
Guthion	2 lb/gal EC	5% NaOH -	5:1 by volume	15 min
	50% WP	50% ethanol	1/2 gal to 1 lb	30 min
Malathion	5 lb/gal EC	5% NaOH -	10:1 by volume	15 min
	WP, D	50% ethanol	1/2 gal to 1 lb	30 min
Carbaryl	4 lb/gal OS	5% NaOH -	10:1 by volume	15 min
	2 lb/gal EC	50% ethanol	10:1 by volume	15 min
	1 lb/gal EC		5:1 by volume	15 min
	WP, D		1 gal to 1 lb	30 min
Captan	WP, D	10% NaOH	1 gal to 1 lb	30 min
Atrazine	WP	10% NaOH	1 gal to 1 lb	48 hr

*EC - emulsifiable concentrate, D - dust, WP - wettable powder, OS - oil solution.

highly toxic degradation products when insufficient water is present. In the disposal of small quantities of naled, diazinon, Guthion, malathion, carbaryl, captan and atrazine, the information provided in Table 7 is to be used in conjunction with the information on recommended personal protection equipment (Table 6) and the Pesticide Disposal Procedure by Alkali Treatment presented in Table 8.

As discussed previously, there are no practical chemical detoxification techniques for the other 13 pesticides investigated. For these pesticides, incineration or burial in a specially designated landfill* are the only environmentally adequate methods of disposal. However, there is a scarcity of both pesticide incinerators and specially designated landfills in operation to serve the farm communities and the general public, and land burial or ground surface disposal are the only other options suitable for the disposal of small quantities of these pesticides. These alternate methods for the disposal of small quantities of the 13 pesticides are given in Table 9. It may be noted that ground surface disposal at herbicidal dosage is recommended for alachlor instead of land burial because at higher concentrations, alachlor could conceivably react with nitrites in the soil to form a nitrosoamine, a suspected carcinogen. Also, acid treatment is recommended for picloram prior to land burial. Picloram is usually formulated as an aqueous solution containing its potassium salt, which is extremely water-soluble, mobile, and persistent in soil. Conversion of the potassium salt of picloram to the acid form by the addition of a mineral acid therefore reduces the potential for water contamination.

For the decontamination of glass and metal pesticide containers, the NACA triple rinse and drain procedure (Appendix D) should be followed whenever applicable. To decontaminate glass and metal containers for naled, diazinon, Guthion, malathion, carbaryl, captan and atrazine, the use of a caustic soda rinse solution is also effective and is recommended

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*"Specially designated landfill" is defined in 40CFR Part 165 as a landfill at which complete long term portection is provided for the quality of surface and subsurface waters from pesticides, pesticide containers, and pesticide-related wastes depositied therein, and against hazard to public health and the environment.

TABLE 8

PESTICIDE DISPOSAL PROCEDURE -
CHEMICAL DETOXIFICATION BY ALKALI TREATMENT

This procedure is only applicable to seven of the 20 pesticides investigated in the present study: naled, diazinon, Guthion, malathion, carbaryl, captan, and atrazine. Do not use this procedure for other pesticides since decomposition products are unknown and may be harmful. The quantity of decontaminant solution to be used in given in Table 7. Note that caustic soda (lye) absorbs moisture and should be stored in a tightened container. The disposal procedure is outlined as follows:

1. Use personal protection equipment (Table 6).
2. Carefully mix water, ethanol (if recommended) and caustic soda (lye) in a container to make up the recommended decontaminant solution (Table 7). Note that the reaction between caustic soda and water generates heat and splattering may occur. To make up 1 gal of the 5% NaOH - 50% ethanol solution, use 1 cup of caustic soda with 2 qts of ethanol and 1-3/4 qts of water. To make up 1 gal of the 10% NaOH solution, use 2 cups of caustic soda with 3-1/2 qts of water.
3. Place pesticide requiring disposal in a 5 gal metal container. The container should be one that has been used for the same type of pesticide or one that has not been previously used for pesticide and other chemicals. Add the recommended amount of decontaminant solution (Table 7) to the pesticide. Do not fill up more than half of the container. Larger quantities of pesticides should be disposed of in several smaller batches.
4. Tighten the bungs and other closures. Rotate the container carefully to promote the mixing between the pesticide formulation and decontaminant solution.
5. Let the container and reaction mixture stand for at least 15 minutes with occasional agitation. Consult Table 7 for the recommended contact time for each pesticide formulation.

TABLE 8 (CONTINUED)

6. Remove all bungs and closures and drain the reaction product mixture into a pit or trench at least 18 inches deep, located in non-crop land away from water supplies. Cover with earth.
7. Flush inside and outside of container with clear water.
8. Tighten all bungs and closures. Puncture the container with a pick axe or chisel and crush immediately and recycle for scrap to a steel melting plant. If container recycle cannot be accomplished, bury the container at least 18 inches deep in an isolated area away from water supplies or at an approved dump site.

TABLE 9

ALTERNATE METHODS FOR THE DISPOSAL OF
SMALL QUANTITIES OF SELECTED PESTICIDES

Pesticide	Disposal Method
Dursban	Land burial
Methyl parathion	Land burial
Maneb	Land burial
Alachlor	Ground surface disposal
Diuron	Land burial
Picloram	Land burial with acid treatment
Trifluralin	Land burial
Methoxychlor	Land burial
Chlordane	Land burial
Toxaphene	Land burial
2,4-D	Land burial
Amiben	Land burial
Pentachlorophenol	Land burial

as an alternate procedure. The caustic soda rinse procedure is described in Table 10. To decontaminate glass and metal containers for other pesticides, the only alternate procedure is the use of a detergent rinse solution as described by Lawless et al.[1] This procedure is identical to the caustic soda decontamination procedure (Table 10) except that no caustic soda is added and the rinse procedure is repeated once. The rinse solution for this procedure contains undegraded pesticides and must be disposed of by, in order of preference: (i) incineration; (ii) burial at an approved landfill; (iii) burial in an isolated area away from water supplies.

The preferred method for the disposal of combustible pesticide containers is by burning in approved incinerators. Included in this category are paper bags, fiber drums, burlap bags, cloth bags, cardboard boxes, fiber boxes, wooden boxes, and plastic bags. If this cannot be accomplished, the containers should be emptied as thoroughly as possible, crushed (if applicable), and buried in approved landfills or at least 18 inches deep in an isolated area away from water supplies. Open burning of the used pesticide containers can be very hazardous and is not recommended. In the case of herbicides, open burning may result in the emission of vapors that could cause damage to nearby vegetation.

Small empty aerosol cans for pesticides should not be incinerated or burned since they may contain explosive amounts of residual hydrocarbon propellant.[1] These can be disposed of either through the household trash collection service or be buried at least 18 inches deep in an isolated area away from water supplies.

TABLE 10

PESTICIDE CONTAINER DECONTAMINATION PROCEDURE
WITH CAUSTIC SODA

This procedure is only applicable to empty glass and metal containers for naled, diazinon, Guthion, malathion, carbaryl, captan and atrazine. Do not use this procedure for containers of other pesticides without consulting the pesticide manufacturer or EPA personnel. The procedure is outlined as follows:

1. Use personal protection equipment (Table 6).
2. Drain container as completely as possible to spray tank or to another container for chemical detoxification. In the latter case, do not mix the pesticide with other types of pesticide formulations. Follow the pesticide detoxification procedure described in Table 8.
3. Carefully add water, detergent and caustic soda (lye) and tighten the bungs and other closures. The amount of rinse solution to be added depends on the container size.
   a. container size less than 5 gal - 1 pt water, 1 tablespoon detergent, 1 teaspoon caustic soda.
   b. 5 gal containers - 2 qt water, 2 tablespoons detergent, 1/2 cup caustic soda.
   c. 15 gal containers - 1-1/2 gal water, 1/4 cup detergent, 1/2 lb (approximately 1 cup) caustic soda.
   d. 30 gal containers - 3 gal water, 1/2 cup detergent, 1 lb (approximately 2 cups) caustic soda.
   e. 55 gal containers - 5 gal water, 1 cup detergent, 2 lb (approximately 4 cups) caustic soda.
4. Rotate the container carefully to wet all inner surfaces with the rinse solution.
5. Let the container stand 15 minutes with occasional agitation.

TABLE 10 (CONTINUED)

6. Remove all bungs and closures and bury the rinse solution at least 18 inches deep in an isolated area away from water supplies.

7. Flush inside and outside of container with clear water.

8. For 30 and 55 gal steel containers, replace closures and secure tightly and send the containers to an approved drum reconditioner (check with State Department of Agriculture for list) or recycle as scrap into a steel melting plant. For 1 gal and 5 gal steel containers, puncture with a pick axe or chisel and crush immediately and recycle for scrap to a steel melting plant. For glass containers break or crush into large container (such as 55 gal open headed drum with cover) and recycle for scrap to a glass melting plant. If container recycle cannot be accomplished, the container should be crushed and buried at least 18 inches deep in an isolated area away from water supplies or at an approved dump site. Do not reuse container.

4. CONCLUSIONS AND RECOMMENDATIONS

The present study has demonstrated that chemical detoxification can be an effective method for the disposal of small quantities of excess pesticides and the decontamination of pesticide containers. A total of twenty pesticides representative of different chemical classes were investigated, and the results of the study indicated that alkali treatment is a practical degradation/detoxification technique for naled, diazinon, Guthion (azinphos-methyl), malathion, carbaryl (Sevin), captan, and atrazine. The effects of chemical treatment on these seven pesticides and the reasons for recommending alkali treatment are summarized in Table 11. Detailed disposal procedures for these pesticides based on alkali treatment have been developed and presented in Section 3.

No practical chemical degradation/detoxification methods were identified for the disposal of Dursban, methyl parathion, maneb, alachlor (Lasso), diuron, picloram, trifluralin, methoxychlor, chlordane, toxaphene, 2,4-D, amiben (chloramben), and pentachlorophenol. In most cases, chemical methods were not recommended at the present time for one or more of the following reasons:

- The extent of chemical degradation is unknown or imcomplete.
- The identity of the degradation products are unknown.
- The environmental hazards of the degradation products are unknown.
- The chemical reagents involved are expensive and hazardous.
- The chemical degradation products are hazardous.

The effects of chemical treatment on the thirteen pesticides and the specific reasons for not recommending chemical treatment are summarized in Table 12. For these pesticides, alternate disposal methods based on land burial, land burial with acid treatment, or ground surface disposal have been proposed and discussed in Section 3. However, with the exception of land burial for trifluralin and possibly for 2,4-D, the other alternate disposal procedures prescribed only result in better containment of the hazard and

TABLE 11

SUMMARY OF EFFECTS OF CHEMICAL TREATMENT ON PESTICIDES FOR WHICH ALKALI TREATMENT IS RECOMMENDED

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazards of Degradation Products
Naled (Dibrom)	Alkaline hydrolysis	Complete degradation	The alkaline salts of dimethylphosphoric acid, hydrobromic acid and dichlorobromoacetic acid formed are nontoxic.
Diazinon	Alkaline hydrolysis	Complete degradation	The alkaline salt of diethythiophosphoric acid and the 2-isopropyl-4-methyl-6-hydroxypyrimidine formed are considerably less toxic than diazinon.
	Acid hydrolysis	Complete degradation	In large excess of water, same hydrolysis products are obtained as in alkaline hydrolysis. However, highly toxic tetraethyl dithio - and thiopyrophosphates have been found with insufficient water in acid medium.
	Chemical oxidation	Complete degradation	Diazoxon formed is equally toxic.
Guthion (Azinphosmethyl)	Alkaline hydrolysis	Complete degradation	The alkaline salt of dimethyldithiophosphoric acid and the anthranilic acid formed are nontoxic.
	Chemical oxidation	Complete degradation	Gutoxon formed is equally toxic.
Malathion	Alkaline hydrolysis	Complete degradation	The alkaline salt of dimethyldithiophosphoric acid formed is nontoxic. The diethyl fumarate formed is not a cholinesterase inhibitor.
	Acid hydrolysis	Slow reaction	The dimethythiophosphoric acid and the 2-mercaptodiethyl succinate formed are not cholinesterase inhibitors.
	Chemical oxidation	Complete degradation	Malaoxon formed is more toxic than malathion.
Carbaryl (Sevin)	Alkaline hydrolysis	Complete degradation	1-Napthol and methyl amine formed have low toxicity. Alkaline carbonate formed is nontoxic.
	Acid hydrolysis	Very slow reaction	Identity and toxicity of products unknown.
	Nitric acid	Unknown	Nitrobenzene and other unidentified products are formed.
Captan	Alkaline hydrolysis	Complete degradation	Tetrahydrophthalimide and alkaline sulfide, chloride and carbonate are formed. Tetrahydrophthalimide is further hydrolyzed to phthalic acid.
	Acid hydrolysis	Unreactive	- -
Atrazine	Strong alkali	Complete degradation	Hydroxyatrazine formed is herbicidally inactive and will further decompose in plants to amines and carbon dioxide.
	Strong mineral acid	Slow reaction	Hydroxyatrazine is formed.
	Weak alkali or acid	Unreactive	- -

TABLE 12

SUMMARY OF EFFECTS OF CHEMICAL TREATMENT ON SELECTED PESTICIDES

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazards of Degradation Products
Dursban (Chlorpyrifos)	Acid or alkaline hydrolysis	Complete degradation	Toxicity of trichlorohydroxypyridine formed unknown.
	Sodium hypochlorite	Complete degradation	Identity and toxicity of products unknown.
Methyl parathion	Acid hydrolysis	Very slow reaction	p-Nitrophenol formed is toxic.
	Alkaline hydrolysis	Complete degradation	p-Nitrophenol formed is toxic.
	Chemical oxidation	Complete degradation	Methyl paraoxon formed is more toxic than methyl parathion for vertebrates.
	Chemical reduction	Unknown	O,O-dimethyl O-4-aminophenyl thiophosphate is nontoxic to animals, but total environmental hazards are not known.
Maneb	Strong acids	Complete degradation	Carbon disulfide evolved could be an explosive and toxicity hazard.
	Hydrolysis in weak acids or alkali	Complete degradation	Ethylene thiourea formed may be carcinogenic.
	Chemical oxidation	Unknown	Ethylenethiuram monosulfide formed may lead to ethylene thiourea.
Alachlor (Lasso)	Hydrolysis by strong acids or alkali	Complete degradation	The secondary amine formed may react with nitrites in the soil to form nitrosoamine, a suspected carcinogen.
Diuron	Boiling with caustic alkalies or mineral acids	Complete degradation	3,4-dichloroaniline and dimethylamine formed are more toxic than diuron.
	Chemical oxidation	Unreactive	--
Picloram	Sodium hydroxide	Unknown	Decarboxylation and partial dechlorination of picloram. Complete identity and toxicity of products unknown.
Trifluralin	Acid or alkaline hydrolysis	Unreactive	--
	Chemical oxidation	Unreactive	--
Methoxychlor	Alkaline hydrolysis	Slow reaction	Environmental hazards of the 1,1-dichloro-2,2-bis (p-methoxyphenyl) ethylene formed are not known.
	Chemical oxidation	Unreactive	--
Chlordane	Alkaline hydrolysis	Unknown	Partial dechlorination leads to the splitting out of one or two chlorine atoms. Environmental hazards of products unknown.

TABLE 12
(CONTINUED)

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazards of Degradation Products
Chlordane (Continued)	Chemical reduction	Substantial degradation	Identity and toxicity of products unknown.
Toxaphene	Alkaline hydrolysis	Partial dechlorination	Identity and toxicity of products unknown.
2,4-D	Prolonged boiling with HBr or HCl	Complete degradation	2,4-Dichlorophenol formed is extremely susceptible to photodecomposition.
	Sodium hypochlorite or gaseous chlorine at pH 3	Complete degradation	Identity and toxicity of products unknown.
	Nitric acid	Unknown	Environmental hazards of the 2,4-dichloro-5-nitrophenoxyacetic acid formed unknown.
	Hydrogen peroxide	Unreactive	--
Amiben (Chloramben)	Acid or alkaline hydrolysis	Unreactive	--
	Chemical oxidation	Unreactive	--
	Sodium hypochlorite	Complete degradation	Identity and toxicity of products unknown.
Pentachlorophenol	Chemical oxidation	Complete degradation	Chloranil formed is a disinfectant.
	Chlorination	Complete degradation	Hexachlorophenols formed are fungicidal.

cannot be considered totally environmentally acceptable. The preferred disposal method for these pesticides is by incineration.

In Table 13, the final recommendations on the disposal of small quantities of each of the twenty pesticides are summarized according to their chemical classification. It may be observed that all the pesticides that are amenable to alkali treatment belong to either the organophosphates, the carbamates, the imides and hydrazides, or the triazines categories. In general, the other pesticides in these categories are also readily decomposed by alkali treatment. It is important to recognize, however, that the nature of the degradation products is highly dependent on the other functional groups constituting the pesticide. It is thus possible to produce degradation products of various degrees and types of hazard when pesticides of the same chemical class are subjected to alkali treatment. The applicability of alkali treatment as a disposal method for pesticides must therefore be assessed on an individual basis.

On the other hand, knowledge of the hazards associated with the chemical disposal of a specific pesticide can often serve as warning against utilizing the disposal method for other pesticides of the same chemical class. For example, it was pointed out that the mildly acidic, neutral or alkaline hydrolysis of maneb would result in the formation of carcinogenic ethylene thiourea. The same hazard is also present when the other derivatives of ethylenebisdithiocarbamic acid, such as zineb and nabam, are subjected to hydrolysis except in strong acid solutions. In the hydrolysis of diuron, the dimethylamine and 3,4-dichloroaniline formed are both of higher mammalian toxicity than diuron. Similarly, in the hydrolysis of other substituted ureas, such as fenuron, monuron and neburon, the dialkylamine and aniline or chloroaniline formed are all of higher mammalian toxicity than the starting pesticide compounds.

As noted from Table 13, chemical treatment is not recommended for any of the halogen-containing pesticides. This is because most of the halogen-containing pesticides are polyhalogenated and it is difficult to remove more than one halogen atom from the pesticide compound by practical chemical methods. Furthermore, the identity and the environmental hazards of the

TABLE 13

SUMMARY OF RECOMMENDED METHODS FOR THE DISPOSAL OF SMALL QUANTITIES OF SELECTED PESTICIDES

	Pesticide Class	Pesticide	Recommended Disposal Method
I.	Phosphorus-containing pesticides		
	Phosphates and phosphonates	Naled	Alkali treatment
	Phosphorothioates	Diazinon	Alkali treatment
	Phosphorothioates	Methyl parathion	Land burial
	Phosphorothioates	Dursban	Land burial
	Phosphorodithioates	Guthion	Alkali treatment
	Phosphorodithioates	Malathion	Alkali treatment
II.	Nitrogen-containing pesticides		
	Carbamates	Carbaryl	Alkali treatment
	Dithiocarbamates	Maneb	Land burial
	Anilides	Alachlor	Ground surface disposal
	Imides and hydrazides	Captan	Alkali treatment
	Ureas and uracils	Diuron	Land burial
	Triazines	Atrazine	Alkali treatment
	Amines	Picloram	Land burial with acid treatment
	Nitro compounds	Trifluralin	Land burial
III.	Halogen-containing pesticides		
	DDT group	Methoxychlor	Land burial
	Chlorophenoxy compounds	2,4-D	Land burial
	Aldrin-toxaphene group	Chlordane	Land burial
	Aldrin-toxaphene group	Toxaphene	Land burial
	Dihaloaromatic compounds	Amiben	Land burial
	Highly halogenated compounds	Pentachlorophenol	Land burial

partially dehalogenated products are almost always unknown. Thus there is a definite need for catalysts that would facilitate the dehalogenation process.

The above discussion and the detailed analysis presented in the Appendices lead to the conclusion that there is presently insufficient information to develop chemical detoxification procedures for most of the pesticides. Consequently, it is recommended that future research be carried out in the following areas:

- Determine the toxicity of the degradation products from the acid and alkaline hydrolysis of Dursban.
- Determine the identity and environmental hazards of the degradation products of Dursban, 2,4-D, and amiben by sodium hypochlorite treatment.
- Determine the rate of alkaline hydrolysis of picloram, methoxychlor, chlordane, and toxaphene, and the identity and environmental hazards of the degradation products.
- Investigate the detoxification of methyl parathion and chlordane by chemical reduction methods.
- Develop inexpensive and safe catalysts for the dechlorination of chlorinated hydrocarbon pesticides.
- Investigate other practical chemical methods for the disposal of maneb, alachlor, diuron, and picloram.
- Determine the identity and environmental hazards of the degradation products from the treatment of organophosphorus and carbamate pesticides by a decontaminant solution of monoethanolamine (MEA) in dipropyleneglycol monomethyl ether (DPGME).
- Expand the study of chemical disposal methods to other pesticides.

APPENDICES

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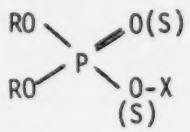
APPENDIX A

CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF PHOSPHORUS-CONTAINING PESTICIDES

A.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

The organophosphorus compounds constitute one of the most important classes of present day pesticides. The scale of use of the organophosphorus pesticides is gradually surpassing that of the organochlorine pesticides because of their lesser persistence in the environment and rapid degradation to supposedly harmless products. In reality, the decomposition of some organophosphorus pesticides may lead to more or equally toxic components. For example, chemical oxidation of parathion leads to the more toxic paraoxon, whereas hydrolysis leads to the equally toxic p-nitrophenol. It is therefore important to know both the identity and the hazard properties of the end degradation products before any chemical detoxification procedure could be recommended.

The organophosphorus pesticide is a tertiary phosphate or thiophosphate ester represented by the general structural formula:



where R is usually an ethyl or methyl group and X is an organic radical. For the organophosphorus pesticides, hydrolysis in many cases results in nontoxic decomposition products and is therefore considered a general detoxification technique for this class of compounds. The hydrolysis could take place in either acid, neutral, or alkaline solutions. In hydrolysis, whether the P-O(S) or (S)O-X bond is ruptured depends on both the structure of the pesticide and the hydrolytic conditions. In alkaline solutions, the P-O(S) bond is broken and the (S)O-X is usually replaced:[14]

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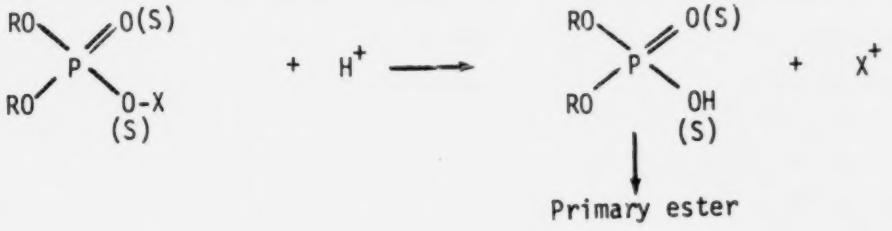
In acid hydrolysis, however, the initial step involves the rupture of the (S)O-X bond, followed by additional hydrolysis of the secondary esters to primary esters:[14]



It should be noted that the cleavage of P-O(S) or the X-O(S) bond also depends on the nature of the X group and the general rule for the acid and alkaline hydrolysis of organophosphorus pesticides described above is not always valid.

The rate of hydrolysis of organophosphorus pesticides under similar conditions is dependent on the chemical nature of the substituents R and X. In general, the substituents that render the phosphorus atom more electropositive also increase the rate of hydrolysis, unless steric effects interfere, thus:[14, 15, 16, 17]

- Pesticides where R is a methyl group hydrolyze more rapidly than their ethyl analogues. For example, methyl parathion hydrolyzes at a faster rate than parathion.

- The substitution of P=O for P=S results in a compound of greater hydrolyzability. For example, paraoxon hydrolyzes at a faster rate than parathion.

This information is useful in prescribing chemical hydrolysis as a detoxification technique, because the alternative of converting the organophosphorus compound to its oxidized product before subjecting to acid or alkaline treatment could be considered. The combined chemical oxidation/chemical hydrolysis detoxification procedure would result in more rapid degradation of the organophosphorus pesticides in many cases.

The rate of hydrolysis of organophosphorus pesticides is also strongly pH dependent. Almost invariably the reaction between an organophosphorus compound and water, acid or base is found to obey second order kinetics, i.e., the rate is proportional to both the concentration of the pesticide and the concentration of the hydroxyl or hydrogen ion.[15, 16] Thus the rate equation can be represented as:

$$\frac{dx}{dt} = k(a-x)(b-x) \qquad (1)$$

where a and b are the initial concentration of the organophosphorus pesticide and the hydroxyl (or hydrogen) ion, respectively; x is the decrease in concentration after time t; k is the reaction rate constant. Integration of the rate equation (1) leads to

$$kt = \frac{1}{b-a} \ln \left[\frac{a}{(a-x)} \frac{(b-x)}{b}\right] \qquad (2)$$

Equation (2) is the fundamental relationship used to determine the time required for the degradation of a specified fraction of an organophosphorus pesticide by hydrolysis. For example, the half-life of an organophosphorus pesticide is given by:

$$t_{0.5} = \frac{1}{k(b-a)} \ln \left[\frac{2b-a}{b}\right] \qquad (3)$$

Similarly, the times required for 99 percent and 99.9 percent hydrolysis of the organophosphorus pesticide are, respectively:

$$t_{0.99} = \frac{1}{k(b-a)} \ln \left[\frac{100b-99a}{b}\right] \qquad (4)$$

$$t_{0.999} = \frac{1}{k(b-a)} \ln \left[\frac{1000b-999a}{b}\right] \qquad (5)$$

In the present study, equations (3), (4) and (5) are used to extrapolate the hydrolysis data reported in the literature to lower or higher pH. This is necessary because most of the studies reported in the literature were concerned with the stability of organophosphorus pesticides at or near neutral pH conditions encountered in the soil or aquatic environment, whereas treatment by strong alkaline or acid solutions is normally recommended for chemical detoxification.

In addition to chemical hydrolysis, the other chemical detoxification procedure of general applicability to organophosphorus pesticides is the use of a decontaminant solution consisting of 12.5 to 25 percent of monoethanolamine (MEA) in a polar, nonaqueous solvent such as dipropyleneglycol monomethyl ether (DPGME). Wolverton et al reported the use of this decontaminant solution to detoxify the organophosphorus pesticides naled, malathion, dichlorvos, fenthion, and TEPP.[18] In the detoxification procedure, ten parts of the decontaminant solution were used to one part of the pesticide, and all the pesticides were completely destroyed in less than two hours with the exception of fenthion. It was also found that the MEA solutions can react with the organophosphorus pesticide by a nucleophilic displacement reaction at phosphorus similar to the hydrolysis reactions, and that the decontamination reaction appeared to follow second order kinetics. In the case of naled and malathion, data from fish studies showed that the mixture containing the pesticide degradation products and the decontaminant solution was relatively nontoxic to mosquito fish, with 48-hour TL_m values of 2100 ppm.

Reactions of organophosphorus pesticides with oxidizing agents generally lead to compounds of higher biochemical activity, although the use of powerful oxidizing agents such as perchloric acid degrade all

the compounds to phosphoric acid.[16] Since perchloric acid solutions may form sensitive powerful explosive mixtures with organic materials and the anhydrous acid decomposes at ambient temperature and explodes on contact with most organic materials, there are no practical chemical oxidation methods to detroxify organophosphorus pesticides directly.

Oxidation or halogenation of organophosphorus pesticides followed by chemical hydrolysis, on the other hand, is a detoxification procedure that deserves special consideration. Both oxidation and halogenation decrease the stability of the organophosphorus pesticide to hydrolysis, although the initial oxidized or halogenated products are generally more toxic. Thus, diazinon may be oxidized to diazoxon which hydrolyzes more readily. In water an access of chlorine rapidly leads to complete breakdown of Schradan to nontoxic compounds, presumably via the hydrolysis of the chlorinated products.[16] Hypochlorites have therefore been used to clean equipment contaminated with Schradan and Dimefox.

A.2 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF NALED

Naled (Dibrom, 0,0-dimethyl 0-2,2-dichloro-1,2-dibromoethyl phosphate) is an active insecticide for the control of both sucking and chewing insects and is manufactured by the bromination of dichlorvos (DDVP). The usual formulations for naled include the 8 lb/gal emulsifiable concentrate (Ortho Dibrom 8 Emulsive) and the 4 percent dust (Ortho Dibrom Dusts).[19]

Naled is stable in brown glass containers but in the presence of metals and reducing agents rapidy loses bromine and reverts to dichlorvos.[3, 20]

$$(CH_3O)_2\overset{O}{\overset{\|}{P}}OCHBrCCl_2Br \longrightarrow (CH_3O)_2\overset{O}{\overset{\|}{P}}\text{-}OCH{=}CCl_2 + Br_2$$

The presence of dichlorvos must therefore be taken into consideration in the recommendation of any detoxification procedure for naled.

With respect to hydrolysis, naled is more stable than dichlorvos. The hydrolysis of naled results in the formation of dimethylphosphoric

acid, hydrobromic acid, and dichlorobromoacetic acid.[21] For dichlorvos, the hydrolysis products are dimethylphosphoric acid and dichloroacetaldehyde.[21, 22] In the presence of NaOH, the sodium salts of the acids would be formed. Since dimethylphosphoric acid and its sodium salt and the sodium salt of dichlorobromoacetic acid are practically harmless, and dichloroacetaldehyde rapidly decomposes and evaporates, no toxic residues would remain from the hydrolysis products of naled and dichlorvos.[21, 23]

The rate of hydrolysis of naled has been reported to be about 10 percent per day in ambient water.[19, 24] Metcalf indicated that naled is destructively hydrolyzed in water in about 2 days.[25] Using the more conservative estimate of 10 percent hydrolysis per day and the bimolecular reaction rate model described in A.1, the time required to degrade 99.9 percent of the naled in a 8 lb/gal formulation with 1 N NaOH was calculated to be less than 0.5 min, when the volume-to-volume ratio of the NaOH decontaminant solution to naled formulation was ten to one. It was also noted that a ten to one volume-to-volume ratio provides approximately 30 percent more than the stoichiometric amount of NaOH required to neutralize the acids formed from the hydrolysis of naled. Since dichlorvos hydrolyses at a faster rate than naled, any dichlorvos resulting from the decomposition of naled in the pesticide formulation would also be hydrolyzed almost instantaneously in the 1N NaOH. For the 4 percent dust formulation of naled, a two to one volume-to-volume ratio of 1 N NaOH solution to naled dust is more than adequate to detoxify the pesticide. In the case of both the emulsifiable concentrate and dust formulations, however, the naled must first be dissolved into the aqueous phase before the neucleophilic attack by the hydroxyl ion can occur. To accomplish this, it is recommended that a ethanol be added to make up a 50 percent ethanol solution in 1N NaOH.[26]

A decontaminant solution containing 12.5 percent of monoethanolamine (MEA) in dipropylene glycol monomethyl ether (DPGME) solvent has also been developed to detoxify naled.[18] In the experiments conducted, 85 percent technical naled was exposed to the decontaminant solution in a volume-to-volume ratio of 10 parts decontaminant to the one part naled.

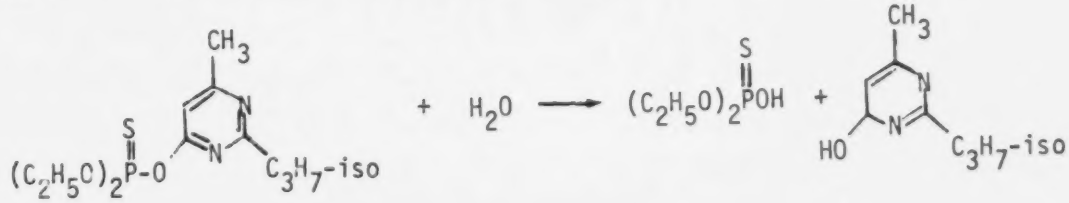
Naled was shown to be destroyed completely after 30 min, and the data obtained from the subsequent fish studies indicated that the reaction product mixture has low toxicity to fish, with a 48-hour TL_m of 2109 ppm for mosquito fish. The MEA-DPGME solution has been used effectively to decontaminate spray equipment for naled and should be applicable to the decontamination of small quantities of naled formulations and used naled containers.

For the decontamination of naled containers, the triple rinse and drain procedure developed by the National Agricultural Chemicals Association (NACA) is recommended (Appendix D). The use of a rinse solution containing caustic soda and detergent may also be considered. These decontamination procedures are described in detail in Section 3.

A.3 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF DIAZINON

Diazinon (0,0-diethyl 0-(2-isopropyl-4-methylpyrimidyl-6) thiophosphate) is used to control various plant pests and animal parasites and is marketed in the form of emulsive concentrates, wettable powders, dusts and granulated formulations. The typical formulations include 5 percent and 10 percent granules (Basudin 5 and Basudin 10), 25 percent and 60 percent emulsive concentrates (Basudin 25 and Basudin 60), and 40 percent wettable powders (Basudin 40).

Diazinon is miscible with ethanol, acetone, xylene, and soluble in petroleum oils. In an excess of water, the principal products of diazinon are diethylthiophosphoric acid and 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMHP) under both acidic and alkaline conditions.[21, 27]



The major hydrolysis product IMHP has an acute oral LD_{50} value of 2700

mg/kg for mice and is considerably less toxic than diazinon.[14] Diethylthiophosphoric acid is also not known to be toxic. Chemical hydrolysis can therefore be considered a possible method for the disposal of diazinon.

The kinetics of hydrolysis of diazinon have been studied by a number of investigators. In a study conducted on aqueous solutions of diazinon with 3.5 percent acetone at concentrations of 100 mg/l, Weiss and Gakstatter determined the half-lives of diazinon as 25, 45 and 40 days at pH, 6, 7 and 8, respectively, under experimental temperature conditions of 18 to 15 C.[28] Ruzicka et al reported the half-life of diazinon at 70 C in ethanol - pH 6 buffer solutions as 37 hours.[15] The 30 percent ethanol was used to improve pesticide solubility. Konrad et al studied the effect of pH on rates of diazinon hydrolysis in aqueous systems.[29] At pH 6 diazinon was found to be quite stable to hydrolysis, but at pH 2 hydrolysis was extremely rapid. Cowart et al found 46.3 percent diazinon remaining after two weeks in a neutral aqueous solution at room temperature.[30] Gomma et al determined the hydrolysis rates of diazinon and diazoxon at five pH values and at a temperature of 20 C.[27] In Table 14, the half-lives of diazinon at different pH values are shown with the calculated bimolecular rate constants for hydrolysis. It is seen that diazinon is quite stable in the pH range of 5.0 to 9.0, although the hydrolysis process is rapid under acidic (pH < 3.1) or alkaline conditions (pH > 10.4). For acid and alkaline hydrolysis, the bimolecular rate constants presented in Table 14 were calculated as:

$$k = \frac{\ln 2}{t_{0.5} \cdot (OH^-)} \qquad \text{for pH} < 7$$

and

$$k = \frac{\ln 2}{t_{0.5} \cdot (H^+)} \qquad \text{for pH} > 7$$

TABLE 14

EFFECT OF pH ON THE HYDROLYSIS
RATE OF DIAZINON AT 20 C

pH	Half-life	Bimolecular Rate Constant (l/mole-hr)	Reference
2.0	83.3 min	49.9	Konrad et al[29]
3.1	706.1 min	74.2	Gomma et al[27]
4.0	31 hr	223.5	Konrad et al
5.0	740.7 hr	93.6	Gomma et al
6.0	25 days	1155.2	Weiss and Gakstatter[28]
6.0	37 hr	18733.7	Ruzicka et al[15]
7.0	45 days	-	Weiss and Gakstatter
7.0	302.5 hr	-	Cowart et al
7.4	4435.8 hr	-	Gomma et al
8.0	40 days	722.0	Weiss and Gakstatter
9.0	3263 hr	21.2	Gomma et al
10.4	144.9 hr	19.0	Gomma et al

where (H^+) and (OH^-) are the hydrogen and hydroxyl ion concentrations and $t_{0.5}$ is the half-life of diazinon at the corresponding pH value. It may also be noted from Table 14 that the value of the rate constant varies under both acidic and alkaline conditions,* indicating either conflicting data or the inadequacy of the bimolecular reaction rate model to describe the chemical hydrolysis of diazinon. On the other hand, the values of the rate constants calculated from the experimental data of Gomma et al do confirm the bimolecular reaction rate model and their data generally provides more conservative estimates for the k values. Using the Gomma et al k values and the bimolecular reaction rate model, the times required to degrade 99.9 percent of the diazinon in the 60 percent and 25 percent emulsive concentrate formulations have been calculated for both acid and alkaline hydrolysis conditions. The results of these calculations are presented in Table 15, and indicate that either 1N HCl or 1N NaOH may be employed as the decontaminant solution to detoxify diazinon, although acid hydrolysis is several times more rapid than alkaline hydrolysis. For practical detoxification of the emulsive concentrates, granular or powder formulations of diazinon, it is recommended that ethanol be added to make up a 50 percent ethanol solution in 1N HCl (or 1N NaOH), as the diazinon must be first dissolved in the aqueous phase before the hydrolysis reaction can occur. Also, a volume-to-volume ratio of ten parts of decontaminant solution to one part of the pesticide formulation is recommended. The large excess of decontaminant solution is essential since small amounts of the highly toxic tetraethyl dithio- and thiopyrophosphates have been found with insufficient water in acid medium.[21] Tetraethyl dithiopyrophosphate (sulfotepp) has an acute oral LD_{50} value of 5 mg/kg for rats, whereas the LD_{50} of tetraethyl monothiopyrophosphate is 0.5 mg/kg.[21]

The effect of temperature on the hydrolysis rate constants has also been determined by Gomma et al.[27] The data agreed with the Arrhenius equation and showed the half-lives of diazinon at 60 C as 46.7 min at

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*However, since the mechanism for acid hydrolysis is different from alkaline hydrolysis, the value of the rate constant for acid hydrolysis is also different from that for alkaline hydrolysis.

TABLE 15

TIME REQUIRED FOR 99.9 PERCENT
DEGRADATION OF DIAZINON AT 20 C
WITH CHEMICAL HYDROLYSIS

Diazinon Formulations	Decontaminant Solution	Volume-to-volume ratio of Decontaminant Solution to Formulation	Time Required for 99.9% Degradation
60% e.c.	1N NaOH	10:1	30.2 min
25% e.c.	1N NaOH	10:1	26.2 min
25% e.c.	1N NaOH	5:1	31.6 min
25% e.c.	1N NaOH	3:1	40.8 min
60% e.c.	1N HCl	10:1	7.8 min
25% e.c.	1N HCl	10:1	6.7 min
25% e.c.	1N HCl	5:1	8.1 min
25% e.c.	1N HCl	3:1	10.5 min

pH 3.1 and 12.4 hr at pH 10.4. However, since the rate of hydrolysis of diazinon is reasonably rapid at 20 C in either 1N HCl or 1N NaOH solution (Table 15), there appears to be no need to further enhance the degradation rate of diazinon by raising the reaction temperature.

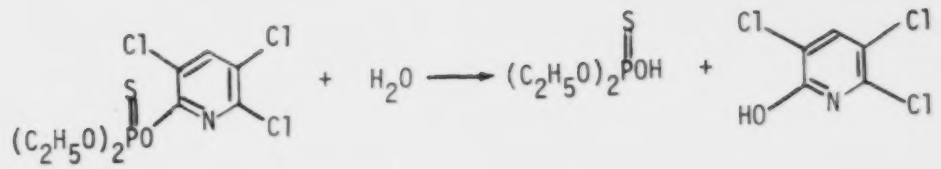
Diazinon is susceptible to oxidation.[20] The oxidized product diazoxon is probably of the same toxicity as diazinon but hydrolyses at a faster rate than diazinon.[27] The hydrolysis products of diazoxon are diethylphosphoric acid and 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMHP).[27] Diethylphosporic acid is nontoxic for both insects and animals and breaks down completely to phosphoric acid, methane, and carbon dioxide under the influence of sunlight.[21] Thus it is possible to detoxify diazinon by first oxidizing the pesticide to diazoxon followed by chemical hydrolysis.

For the decontamination of diazinon containers, both the NACA triple rinse and drain procedure (Appendix D) and the use of a rinse solution containing caustic soda and detergent may be considered. The details of these decontamination procedures, including the proper disposal of rinse solutions and decontaminated containers, are described in Section 3.

A.4 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF DURSBAN

Dursban (chlorpyrifos, 0,0-diethyl 0-3,5,6-trichlopyridyl thiophosphate) is an active insecticide for the control of sucking and chewing plant pests as well as household parasites. The usual formulations include the 2 and 4 lb/gal emulsifiable concentrates (Dursban 2E and Dursban M), the 0.5 to 15 percent granules, and a number of other oil-soluble (Dursban 6, Dow Mosquito Fogging Concentrate) and water emulsifiable formulations (Dursban 21D).

Dursban has very low solubility in water but is readily soluble in most organic solvents (e.g. 63 g/100 g ethanol at 25 C).[31] Dursban is stable under normal storage conditions. In acid or alkaline media the compound is slowly hydrolyzed by water, forming diethylthiophosphoric acid and trichlorohydroxypyridine.[21]



Although diethylthiophosphoric acid is not biologically active and breaks down eventually to phosphoric acid, thiophosphoric acid and ethanol, toxicity data on trichlorohydroxypyridine are not readily available. For comparison, the acute oral LD_{50} values for mouse have been given as 235, 1150, and 430 mg/kg for the pentachloro-, 2,3,5,6-tetrachloro- and 2,3,5-trichloropyridine, respectively.[32]

The half-lives of Dursban in phosphate buffer solutions at 25 C have been reported to be 63, 35 and 23 days at pH values of 5, 7 and 8 respectively.[31] With respect to temperature, the hydrolysis rate increases approximately 3-fold for every 10 C rise, and the half-life of Dursban at pH 7 and 35 C is reduced to 12 days.[23] The temperature effect on hydrolysis rate can be represented by an energy of activation of 19,500 cal/mole-K for the hydrolysis reaction, and the half-life of Dursban at pH 7 and 100 C can be calculated as 66.5 min.

In aqueous methanoic solution, the half-life of Dursban is 1,930 days at pH 6.0 and 7.2 days at pH 9.96.[20] Using this information and the bimolecular reaction rate model, the time required to degrade 99.9 percent of the Dursban in a 4 lb/gal formulation with a 1N NaOH-methanol solution was calculated to be 12 min, when the volume-to-volume ratio of the decontaminant solution to Dursban formulation was 10 to 1.

Spray mixtures containing less than 1 percent Dursban have been destroyed with an excess of 5.25 percent sodium hypochlorite in less than 30 min at 100 C and in 24 hours at 30 C.[1] For concentrated mixtures containing 61.5 percent Dursban, the active ingredient was essentially destroyed by treatment with 100 volumes of the 5.25 percent sodium hypochlorite solution and steam in 10 min.[1] However, no information was given on the identity and toxicity of the degradation products.

In summary, either the 1N NaOH-methanol solution or the 5.25 percent sodium hypochlorite solution and steam may be used to degrade but not necessarily detoxify Dursban. The identity and toxicity of the degradation products must be established before either method can be recommended as the detoxification procedure for Dursban. For small spills or leaks, Dow recommends absorption with materials such as sand and bury the cleaned up waste in locations away from domestic water supplies.[33] For large spills, Dow recommends barricading the area, elimination of ignition sources and consult the manufacturer.[33]

For the decontamination of Dursban containers the NACA triple rinse and drain procedure (Appendix D) is recommended. The use of a caustic soda - methanol or caustic soda - detergent rinse solution will also be effective in decontaminating the container, but the rinse solutions must be disposed of either by incineration or burial in an area away from water supplies.

A.5 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF METHYL PARATHION

Methyl parathion (O,O-dimethyl O-4-nitrophenyl thiophosphate) is used for the control of a wide variety of plant pests and is gradually displacing parathion because of its lower toxicity for mammals. The usual formulations are emulsions (up to 7.5 lb/gal), wettable powders and dusts (1 and 2 percent).

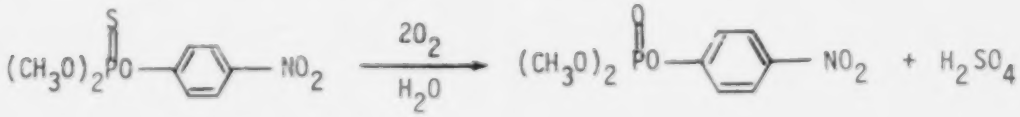
Methyl parathion is slightly soluble in paraffinic hydrocarbons but highly soluble in aromatic hydrocarbons and most organic solvents. It is hydrolyzed by water and in alkaline medium with the formation of dimethylthiophosphoric acid and p-nitrophenol:

Dimethylthiophosphoric acid or its sodium salt are not chlolinesterase inhibiting materials and may undergo further decomposition. The p-nitrophenol formed, however, has an intravenous LD_{50} of 10 mg/kg for dogs and is within the same range of toxicity as methyl parathion.[14]

The rate of hydrolysis of methyl parathion has been investigated rather extensively. Melnikov reported that at pH 1-5, 50 percent of the methyl parathion is hydrolyzed in 175 days at 20 C and the rate of hydrolysis in alkaline medium is still greater.[21] Gunther and Blinn reported the half-life of methyl parathion as 210 min in 0.01 N NaOH at 30 C and 32 min in 1N NaOH at 15 C.[34] Ketelaar and Ketelaar and Gersmann studied the alkaline hydrolysis of methyl parathion in water and in 50 percent acetone and derived Arrhenius expressions for the bimolecular reaction rate constants.[35, 36] The half-life of methyl parathion calculated from these rate constants is 4.4 min in 1N NaOH at 20 C and 10.7 min in a mixture of 1N NaOH and 50 percent acetone at 20 C. Muhlmann and Schrader reported the half-life of methyl parathion at 70 C as 15.4 hr at pH 1 and 1.5 hr at pH 9.[22] At 70 C in a 20 percent ethanol - pH6 buffer solution, the half-life of methyl parathion was found to be 8.4 hr.[15] Cowart et al found 43.5 percent methyl parathion remaining after two weeks in a neutral aqueous solution at room temperature.[30]

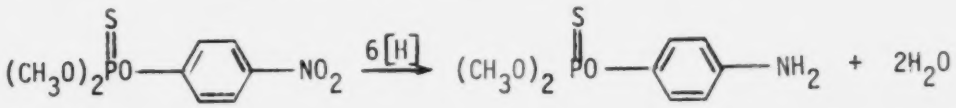
The above information indicates that methyl parathion is hydrolyzed readily in 1N NaOH solution. Alkaline treatment is often the recommended procedure for decontamination of glass and metal containers and clean up of accidental spills and leaks associated with methyl parathion.[10-12, 37-39] Presumably, the pesticide residues will undergo hydrolysis and detoxification in the strong alkali mixture. However, as has been pointed out, the p-nitrophenol formed is equally toxic and the container rinse solutions or the scrubbing and absorption material for spills and leaks must either be incinerated or be buried in an area away from water supplies.

Oxidizing agents convert methyl parathion to O,O-dimethyl O-4-nitrophenyl phosphate (methyl paraoxon) which has an oral LD_{50} of 21 mg/kg for mouse and is more toxic for vertebrates than the starting methyl parathion:[21, 32]



In a $KMnO_4$-parathion system, 2,4-dinitrophenol and paraoxon have been isolated.[14] Similarly, both 2,4-dinitrophenol and methyl paraoxon would be found in a $KMnO_4$-methyl parathion system. 2,4-Dinitrophenol has an oral LD_{50} of 30 mg/kg for rats and is approximately the same toxicity as methyl parathion. Thus, chemical oxidation of methyl parathion leads to degradation products of equal and higher toxicity and is therefore not an acceptable disposal method.

Reducing agents (e.g., metals in acid medium) convert methyl parathion to the corresponding amino compound:[21]



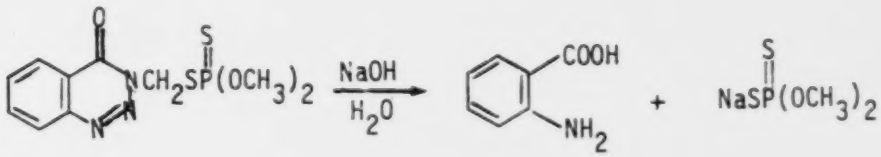
The O,O-dimethyl O-4 aminophenyl thiophosphate formed is nontoxic to animals and does not have an insecticidal effect.

In summary, it may be concluded that both chemical hydrolysis and oxidation result in the formation of toxic products and neither is recommended as a disposal method for methyl parathion. The reduction of methyl parathion by a decontaminant solution of metal in acid medium (e.g. zinc in 9 to 1 mixture of acetic and hydrochloric acid) is a potential chemical detoxification procedure and warrants further investigation. For the decontamination of glass and metal containers, the triple rinse and drain procedure developed by NACA is recommended (Appendix D). Stauffer recommends the use of an aqueous solution of commercial low-foaming hard water detergent (e.g. Tide, Cheer) in 5 percent trisodium phosphate or a solution of 14 weight percent bleach (an aqueous solution of calcium or sodium hypochlorite) for drum decontamination.[38,39] The volume of decontaminant solution recommended by Stauffer is 2 gal for 55 gal drums and 0.5 gal for 5 gal cans. Kerr-McGee recommends the use of a solution of 5 gal water, 1 cup detergent, and 2 lb caustic soda for the decontamination of a 55-gal drum.[12] All three types of decontamination solutions will be effective in decontaminating the methyl parathion container, but the rinse solutions now contain toxic degradation products and must be disposed of by proper incineration or burial in an area away from water supplies.

A.6 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF GUTHION

Guthion (azinphosmethyl, O,O-dimethyl S-(3,4-dihydro-4-keto-1,2,3-benzotriazinyl-3-methyl) dithiophosphate) is an insecticide used for the control of various pests on cotton, fruits, and many other crops. It is marketed as a 50 percent wettable powder and two 2 lb/gal liquid formulations (Guthion 2S and Guthion 2L).

Guthion is soluable in most organic solvents and is chemically stable under ordinary storage conditions. In alkaline medium the main products of Guthion hydrolysis are anthranilic acid and the salt of dimethyldithiophorphoric acid:[24, 40]



The anthranilic acid is a relatively nontoxic substance which occurs naturally in such foods as grapes, cabbage, etc.[40] The sodium salt of dimethyldithiophosphoric acid is not a cholinesterase inhibiting material and will undergo further oxidation and desulfurization reactions to methanol, methane, sodium dithiophosphate, sodium thiophosphate, sodium phosphate and other nontoxic products. Alkaline hydrolysis can therefore be considered as a possible method for the disposal of Guthion.

Muhlmann and Schrader studied the effects of pH on the rate of hydrolysis of Guthion and Gutoxon (the oxygen analogue of Guthion) at 70 C and the effects of temperature on the rate of hydrolysis in the pH 1-5 range.[22] As indicated in Table 16, Guthion hydrolysis is slower under acid conditions than under alkaline conditions. In the pH 1-5 range, the activation energy for Guthion hydrolysis was calculated to be 23,900 cal/mole from the rate constants reported by Muhlmann and Schrader. Since the activation energy for acid hydrolysis is ususally a lot higher than the activation energy for alkaline hydrolysis, the half-life of Guthion at pH 9 and 20 C can be estimated from the calculated activation energy for acid hydrolysis and the data presented in Table 16 as:

TABLE 16

EFFECTS OF pH ON THE RATE
OF HYDROLYSIS OF GUTHION
AND GUTOXON AT 70 C

pH	Half-life of Guthion (hr)	Half-life of Gutoxon (hr)
1.0	24	4.5
2.0	13.5	4.5
3.0	9	4.5
4.0	7.2	4.0
5.0	8.9	4.4
6.0	7.5	4.0
7.0	4.8	2.1
8.0	2.4	0.9
9.0	0.6	-

$$t_{0.5}(\text{pH9, 20C}) < 0.6\, e^{\frac{23900}{1.9872}\left(\frac{1}{293.16} - \frac{1}{343.16}\right)} \text{ hr}$$

$$= 237 \text{ hr}$$

Using the bimolecular reaction rate model, the half-life of Guthion at pH 14 and 20 C was calculated to be less than 0.14 min, and the bimolecular rate constant was calculated to be greater than 4.8 l/(mole-min). For the 2 lb/gal formulation, it was also determined that the time required to degrade 99.9 percent of the Guthion with a 1N NaOH solution was approximately 2 min, when the volume-to-volume ratio of the 1N NaOH decontaminant solution to the Guthion formulation was five to one. In general, these calculations have confirmed Chemagro's statement that Guthion is very sensitive to alkaline hydrolysis and the reaction proceeds rapidly at room temperature.[40] Also, since the alkaline hydrolysis reaction only takes place in the aqueous phase, it is recommended that ethanol be added to make up a decontaminant solution of 50 percent ethanol in 1N NaOH, as Guthion has very low solubility in water.

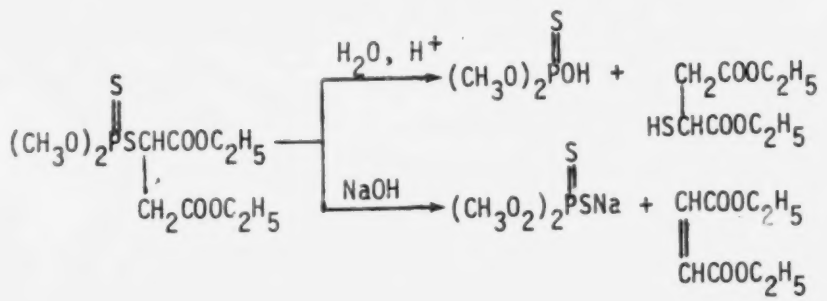
The action of oxidizing agents on Guthion causes splitting off of the thiono sulfur and formation of its oxygen analogue Gutoxon. As noted from Table 16, Gutoxon is more rapidly hydrolyzed than Guthion under both acid and alkaline conditions. In a 1N NaOH solution, the principal products of Gutoxon hydrolysis would be anthranilic acid and the sodium salt of dimethylthiophosphoric acid. Thus chemical oxidation followed by alkaline treatment may be considered as an alternate detoxification procedure for Guthion, although this leads to unnecessary complications as Guthion is rapidly hydrolyzed by cold alkaline solutions.

For the decontamination of glass and metal containers for Guthion, both the NACA triple rinse and drain procedure (Appendix D) and the procedure recommended by Chemagro may be considered. The Chemagro procedure involves the use of a rinse solution containing caustic soda and detergent.[13] The quantity of the chemicals and rinse solutions recommended as well as the proper decontamination procedure are described in detail in Section 3.

A.7 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF MALATHION

Malathion (O,O-dimethyl S-1,2-dicarboethoxyethyl dithiophosphate) is a non-systemic insecticide with a wide range of agricultural and horticultural uses. It is marketed in the form of 5 lb/gal emulsifiable concentrates, 25 and 50 percent wettable powders, and 4 percent dust.

Malathion is miscible with most organic solvents though of limited solubility in petroleum oils. Hydrolysis of malathion follows different paths in acid and alkaline medium. In acid medium the main products of hydrolysis are dimethylthiophosphoric acid and 2-mercaptodiethyl succinate, while in alkaline medium the salt of dimethyldithiophosphoric acid and diethyl fumarate are formed:[14, 21, 22]



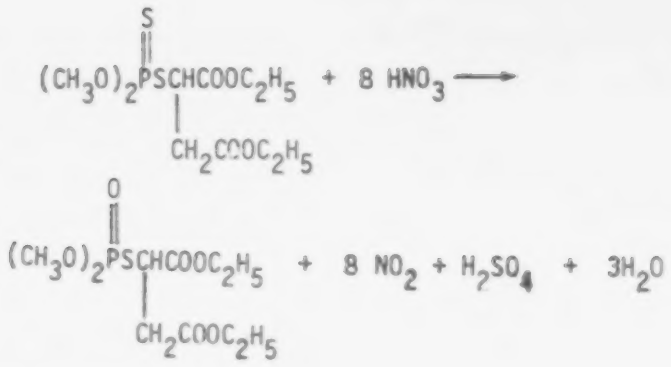
Dimethylthiophosphoric and the sodium salt of dimethyldithiophosphoric acid are not cholinesterase inhibiting materials and will undergo further degradation to other nontoxic products. 2-Mercaptodiethyl succinate has an oral LD_{50} of 1156 mg/kg for rats and diethyl fumarate has an oral LD_{50} of 1780 mg/kg for rats.[32] Although the 2-mercapoto-diethyl succinate and diethyl fumarate formed are within the same range of mammalion toxicity as malathion, neither are cholinesterase inhibitors and both compounds should be relatively nontoxic to insects and fish. Thus, either acid or alkaline hydrolysis may be considered as acceptable methods for the disposal of malathion.

The rate of hydrolysis of malathion has been extensively investigated. Yost et al reported that malathion hydrolysis is almost instantaneous at pH 12, whereas at pH 9 50 percent of malathion was hydrolyzed in 12 hr.[41] At pH 5-7, however, no hydrolysis was observed over a period of 12 days.[42]

Ketelaar and Gersmann studied the alkaline hydrolysis of malathion and derived an Arrhenius expression for the bimolecular reaction rate constant. The activation energy was determined to be 24,500 cal/mole and the bimolecular rate constant at 20 C was 154.5 l/(mole-min).[36] Ruzicka et al found the half-life of malathion in a 20 percent ethanol-pH 6 buffer solution at 70 C to be 7.8 hr.[15] Konrad et al reported that malathion hydrolysis did not occur in acid systems of pH>2, was slow at pH 9 (25 percent degradation in 7 days) and rapid at pH 11 (> 99 percent in 1 day).[43] Cowart et al found 59.3 percent malathion remaining after 7 days in a neutral aqueous solution at room temperature.[30] Malathion is therefore resistant to hydrolysis in neutral or acidic solutions. In a 1N NaOH solution, however, the time required to degrade 99.9 percent of the malathion in a 5 lb/gal formulation was calculated to be less than a minute, when the volume-to-volume ratio of the decontaminant solution to malathion formulation was ten to one. In practice, it is recommended that a 50 percent ethanol-1N NaOH mixture be used as the decontaminant solution, as the alkaline hydrolysis reaction only takes place in the aqueous phase and the solubility of malathion in water is relatively low.

Wolverton et al have reported the use of a decontaminant solution containing 25 percent monoethianolamine (MEA) in dipropylene glycol monomethyl ether (DPGME) solvent to detoxify malathion.[18] For the decontamination of malathion, 95 percent technical malathion was exposed to the decontaminant solution in a volume-to-volume ratio of 10 parts decontaminant to one part malathion. Malathion was shown to degrade completely in 120 min. Also, data from the fish toxicity studies indicated that the reaction product mixture is relatively nontoxic to fish, with a 48-hour TL_m of 2182 ppm for mosquito fish, as compared to malathion's 48-hour TL_m of 0.02 ppm for fish. In addition, it was shown that the detoxification of malathion by MEA took place by a nucleophilic displacement reaction at phosphorus, with a bimolecular reaction rate constant of 0.0160 l/(mole-min).

When malathion is oxidized by nitric acid or other strong oxidizing agents the thiono sulfur atom is split off and the corresponding ester of thiolophosphoric acid (malaoxon) is formed:[21]



Malaoxon is a cholinesterase inhibitor that is more toxic than malathion.[17] Chemical oxidation is therefore not recommended as a disposal method for malathion.

In a study conducted by Kennedy et al, malathion was treated with a mixture of liquid ammonia and metallic sodium or lithium.[44] In either solutions 100 percent degradation of the malathion was obtained. However, the chemical reagents used were dangerous and the identity and toxicity of the reaction products were unknown. For these reasons, the liquid NH_3-Na or NH_3-Li system cannot be considered in any practical disposal procedure.

For the decontamination of malathion containers, both the NACA triple rinse and drain procedure (Appendix D) and the procedure recommended by American Cyanamid may be considered. The American Cyanamid procedure involves the use of a rinse solution containing caustic soda and detergent and is similar to the procedure prescribed by Chemagro for organophosphorus pesticides.[45] The container decontamination procedure is described in detail in Section 3.

APPENDIX B

CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF NITROGEN-CONTAINING PESTICIDES

B.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

The nitrogen-containing pesticides have been broadly classified into the following groups with representative pesticides from each group:

- Carbamates, thiocarbamates and dithiocarbamates - carbaryl, maneb
- Amides, anilides, imides, and hydrazides - alachlor, captan
- Ureas and uracils - diuron
- Triazines - atrazine
- Amines, nitro compounds, quaternary ammonium compounds - picloram, trifluralin

Unlike the organophosphorus pesticides, the nitrogen-containing pesticide subclasses are different from each other in chemical structures and in decomposition chemistry. There are no chemical disposal methods with universal applicability to the nitrogen-containing pesticides. The disposal methods applicable to each subclass of nitrogen-containing pesticides will be discussed along with the chemical degradation/detoxification methods for the representative pesticide from each subclass.

B.2 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF CARBARYL

Carbaryl (Sevin, naphthyl N-methylcarbamic acid) is a versatile insecticide used to control pests of cotton, vegetables and fruit crops. The common formulations include the 50 percent, 80 percent and 85 percent wettable powders (Sevin 50 W, Sevin 80 Sprayable, and Sevin 85 Sprayable), the 2 to 50 percent dusts, the 5 to 10 percent granules, the 1 to 2 lb/gal emulsifiable concentrates, and the 4 lb/gal oil formulation (Sevin 4 Oil).[46]

Carbaryl is highly soluble in organic solvents. In alkaline medium carbaryl is hydrolyzed to 1-naphthol, methyl amine, and the alkaline carbonate:[21]

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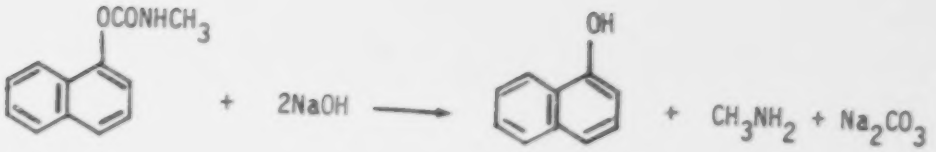


1-Naphthol has an acute oral LD_{50} of 2590 mg/kg for rats. Methyl amine has an acute oral LD_{50} of 2500 mg/kg for rats. However, 1-naphthol is more toxic than carbaryl to young clams and fish.[47] It is also known that 1-naphthol is unstable in the alkaline environment of sea water and degrades to carbon dioxide and numerous other products.[47] The main decomposition product is a precipitate containing a stable free radical that is toxic to certain estuarine species. Therefore alkaline treatment of carbaryl must be followed by burial of the reaction solution in a location away from water supplies.

The alkaline hydrolysis of other esters of carbamic acid follows the same path as carbaryl:

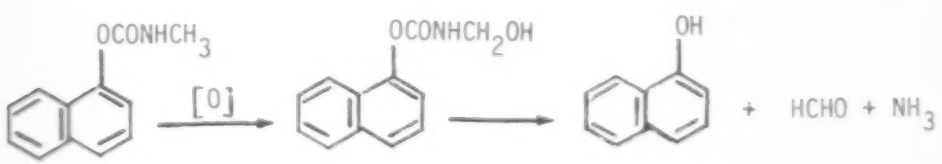
$$ROCNR'' + 2NaOH \longrightarrow ROH + R'NR'' + Na_2CO_3$$

where the products are a hydroxy compound, an amine, and sodium carbonate. The nature of these hydrolysis products is dependent on the R, R' and R" groups. It is thus possible to produce several hydrolysis products of various degrees and types of hazard. The applicability of alkali treatment as a disposal method for carbamate pesticides must therefore be assessed on an individual basis.

Carbaryl is known to be rapidly hydrolyzed in strong alkali.[46] In a study conducted by Karinen et al, the amount of carbaryl hydrolyzed by sea water (at pH 8) in four days was found to be 44 percent at 17 C, 55 percent at 20 C, and 93 percent at 28 C.[48] Aly and El-Dib investigated the hydrolysis of carbaryl in NaOH solution and found the rate of hydrolysis to be first order with respect to the hydroxyl ion concentration.[49] The observed half-lives and the calculated bimolecular rate

constants reported by Aly and El-Dib are given in Table 17, along with the values reported by Wauchope and Hague in a later study.[50] At 20 C, the bimolecular rate constants for alkaline hydrolysis of carbaryl as calculated from the data of Karinen et al, Aly and El-Dib, and Wauchope and Hague are 140, 152, and 195 l/(mole-min), respectively. These values are in reasonably good agreement with each other. Using the bimolecular reaction rate model, the time required to degrade 99.9 percent of the carbaryl in a 4 lb/gal formulation with 1N NaOH was calculated to be less than a minute, when the volume-to-volume ratio of the NaOH decontaminant solution to carbaryl formulation was ten to one. In practice, it is again recommended to use a 50 percent ethanol - 1N NaOH mixture as the decontaminant solution, as the solubility of carbaryl in water is relatively low. For the treatment of carbaryl manufacturing wastes, NACA has recommended the addition of 2 lb of flake caustic (sodium hydroxide) for each 5 lb of actual carbaryl and allow about 24 hours for completion of the reaction.[51] However, the amount of caustic recommended by NACA is only approximately stoichiometric and at least a 50 percent excess should be used. Also, the reaction time of 24 hours appears to be excessively long.

Carbaryl is stable for weeks in weakly acidic solutions. Kennedy et al reported that hydrogen peroxide treatment had no significant effect on carbaryl.[52] Nitric acid treatment, on the other hand, was found to induce changes in carbaryl and lead to the formation of nitrobenzene, along with other unidentified products. In the study of the decomposition of carbaryl in plants and animals, it has been established that oxidation is directed primarily at the methyl group attached to the nitrogen atom:[21]



Also formed as metabolites are 4-hydroxy- and 5-hydroxynaphthyl N-methylcarbamates, which further breakdown with rupture of the aromatic ring. However, the chemistry of the oxidation process as well as the identity

TABLE 17

EFFECTS OF pH AND TEMPERATURE ON
THE HYDROLYSIS RATE OF CARBARYL

pH	Temperature (C)	Half-life	Bimolecular rate constant 1/(mole-min)	Activation energy (cal/mole)	Reference
8.0	17	115.2 hr	100		
8.0	20	84 hr	140	24,090	Karinen et al[48]
8.0	28	24 hr	460		
10.954	3	32 min	24.2		
10.954	13	11 min	69.1		
10.954	23	3.8 min	204	16,900	Aly and El-Dib[49]
10.954	33	1.4 min	537		
10	12	99 min	70		
10	25	20 min	340		
10	35	8 min	900		
9.8	25	27 min	430	19,390	Wauchope and Hague[50]
9.5	25	58 min	380		
9.2	25	116 min	380		
9.0	25	173 min	400		

of the reaction products are not well known. Chemical oxidation therefore cannot be considered as a disposal method for carbaryl.

Under the influence of sunlight, the reversal reaction of carbaryl to 1-naphthol and methylisocynate ($CH_3N=C=O$) has been found to take place.[53] Methylisocynate is a poisonous and highly reactive substance. Accordingly, carbaryl should always be submitted to alkaline hydrolysis before disposal.

For the decontamination of carbaryl containers, both the NACA triple rinse and drain procedure (Appendix D) and the use of a rinse solution containing caustic soda and detergent may be considered. The latter procedure is described in detail in Section 3.

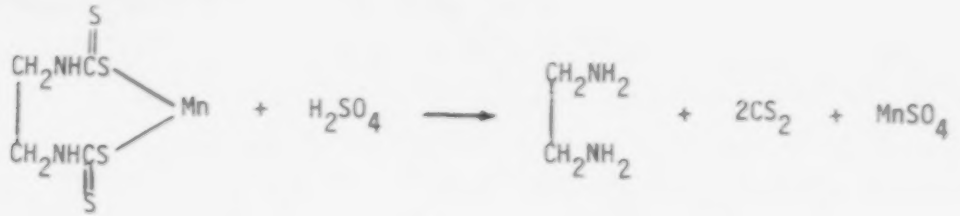
B.3 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF MANEB

Maneb (manganese ethylenebisdithiocarbamate) and its related compounds form the group of dithiocarbamate fungicides which are the most widely used and most versatile of organic fungicides. The other important fungicides in the dithiocarbamate group are zineb, nabam and ferbam. Zineb and nabam are the zinc and disodium salts of ethylenebisdithiocarbamic acid, whereas ferbam is the iron salt of dimethyldithiocarbamic acid.

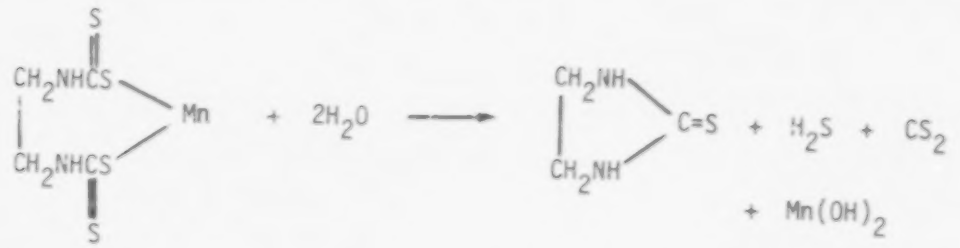
The common formulations of maneb include the following:[54,55]

- Dithane M-45 - a coordination product of zinc ion and manganese ethylenebisdithiocarbamate containing 16 percent manganese ion, 2 percent zinc ion and 62 percent ethylenebisdithiocarbamate ion
- Dithane M-22 Special - a wettable powder containing 80 percent maneb and 20 percent inert ingredients including zinc sulfate
- Manzate - an 80 percent maneb wettable powder
- Manzate D - an 80 percent maneb wettable powder containing zinc
- Tersan LSR turf fungicide - an 80 percent maneb wettable containing zinc

Thus all the maneb formulations are 80 percent wettable powders with or without zinc. There is no practical solvent for maneb, although the compound has very slight solubility in water and in some organics.
The hydrolysis of maneb in either acid or alkaline medium is a rather complex, multi-step process. In the presence of strong acids, maneb decomposes with the formation of ethylene diamine, carbon disulfide and a manganese salt:[25]



In the presence of weak acids, however, the hydrolysis of maneb follows a different path, leading to the formation of ethylene thiourea, hydrogen sulfide, carbon disulfide and manganese hydroxide:[56,57]



In neutral pH or alkaline sultions, the initial organic product is ethylenethiuram monosulfide, which can polymerize to polyethylenethiuram monosulfide or further hydrolyze to ethylene thiourea.[56,58,59] Ethylene diisothiocyanate and ethylene diamine have also been reported.[25, 59] Also, alkaline hydrolysis is accompanied by the evolution of carbon disulfide, but not of hydrogen sulfide.[56] Presumably under these conditions the sulfide sulfur remains in solution, possibly as the alkaline sulfide, and is later oxidized by atmospheric oxygen to the sulfate.

The ethylene thiourea formed under mildly acidic, neutral, or alkaline conditions is of special concern because it has been shown to be

carcinogenic to mammals.[60] Hence all the derivatives of ethylenebis-dithiocarbamic acid are potential sources of carcinogenic products when subjected to hydrolysis except in strong acid solutions. Even the use of a strong mineral acid to dispose of maneb, however, results in the formation of carbon disulfide, a gas which could produce an undesirable explosive and toxicity hazard. Disposal of maneb by either acid or alkaline hydrolysis is therefore not recommended.

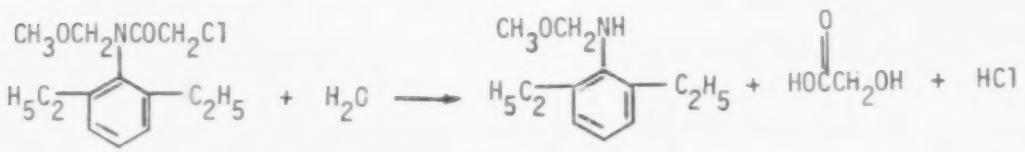
In the oxidation of maneb, ethylenethiuram monosulfide has been identified as one of the products.[25, 58] The ethylenethiuram monosulfide formed may again be further hydrolyzed to ethylene thiourea. Chemical oxidation is therefore not considered as a disposal method for maneb.

For the disposal of small quantities of maneb formulations, burial at least 18 inches deep in non-crop land away from water supplies is recommended. The best method for the disposal of maneb (and other dithiocarbamates) and maneb containers (usually in fiber drums or bags) is incineration in a carefully-operated, well-designed incinerator. The guidelines for maneb disposal by incineration are presented in the Rohm and Haas Pesticide Disposal Manual.[54]

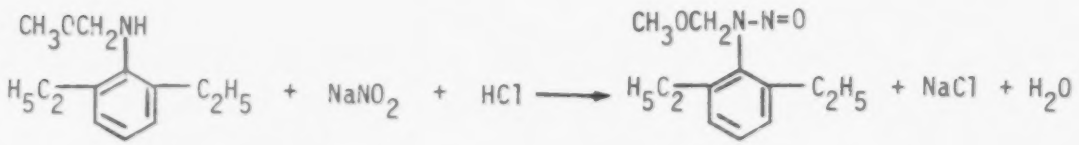
B.4 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF ALACHLOR

Alachlor (Lasso, 2-chloro-N-(2,6-diethylphenyl)-N-methoxymethylacetamide) is a selective pre-emergence herbicide for the control of annual grasses and broad-leaved weeds in crops. The usual formulations are the 15 percent granules.

Alachlor is slightly soluble in water. It is hydrolyzed under strongly acid or alkaline conditions to form a secondary amine and glycollic acid:[25, 61]



In the application of alachlor at herbicidal dosage, the reaction products obtained from its decomposition in the soil are the same as the hydrolysis products and neither the secondary amine nor the glycollic acid is toxic to plants in the amounts released.[61] Glycollic acid has an oral LD_{50} of 3200 mg/kg for rats and is therefore relatively nontoxic to mammals.[32] However, the secondary amine product is of concern because it could conceivably react with nitrites in the soil to form a nitrosoamine, a suspected carcinogen:



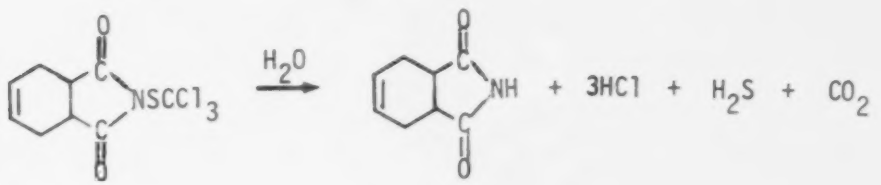
At high application rates, CDAA (Randox), a chloroacetamide herbicide similar to alachlor, has been found to inhibit the transformation of nitrite to nitrate in soil, although at herbicidal dosage this is not significant.[61] The inhibition mechanism could be due to the reaction of the secondary amine from CDAA hydrolysis with the nitrite to form nitrosoamines.

Lawless et al recently indicated a different set of hydrolysis products from the treatment of alachlor by strong acid or alkaline solutions, where chloroacetic acid, methanol, formaldehyde and 2,6-diethylaniline were obtained.[1] The chloroacetic acid would lead to glycollic acid under further hydrolysis, and the 2,6-diethylaniline, being a primary amine, would not form nitrosoamines with nitrites. 2,6-Diethylaniline has an oral LD_{50} of 2030 mg/kg for rats.[32] However, since alachlor has a relatively low mammalian toxicity and leads to soil decomposition products that are nontoxic to plants when applied at herbicidal dosage, the recommended method for the disposal of small quantities of alachlor is by landspreading at herbicidal dosage. For the disposal of larger quantities of alachlor, incineration should again be considered. For the decontamination of alachlor containers, the NACA triple rinse and drain procedure (Appendix D) is the only recommended method. The rinse solution should be disposed of by addition to the spray tank.

B.5 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF CAPTAN

Captan (N-trichloromethylthiotetrahydrophthalimide) is a broad-spectrum protective fungicide employed for the control of various diseases of agricultural crops, including seed disinfection. It is marketed in the form of 50 and 80 percent wettable powder, 5 and 10 percent dusts, and 25 to 75 percent dusts and wettable powder for seed treatment.

Captan is hydrolytically stable at neutral or acid pH but decomposes fairly rapidly in alkaline media, resulting in the formation of tetrahydrophthalimide, hydrogen chloride, hydrogen sulfide, carbon dioxide, and possibly elemental sulfur:[21, 62]



Tetrahydrophthalimide is capable of further hydrolysis to phthalic acid.[21] In the presence of strong alkaline solution such as NaOH, sodium chloride, sodium sulfide and sodium carbonate will be formed. Thus the alkaline treatment of captan leads to the formation of nontoxic degradation products and may be considered as an environmentally acceptable disposal method.

Daines et al reported that lime completely destroyed the fungicidal activity of captan.[62] Laboratory studies conducted on an aqueous slurry of captan indicated that the rate of captan decomposition was very rapid at pH 10.6 and instantaneous at pH 14. For the treatment of large spills associated with captan or equipment decontamination, Stauffer recommends the use of an aqueous solution of commercial low-foaming, hard water detergent (Tide, Cheer, etc) in 5 percent trisodium phosphate or 10 to 25 percent sodium hydroxide.[63] Captan is usually packed in 2 lb to 50 lb bags. The empty bags should be buried in an isolated area away from water supplies.

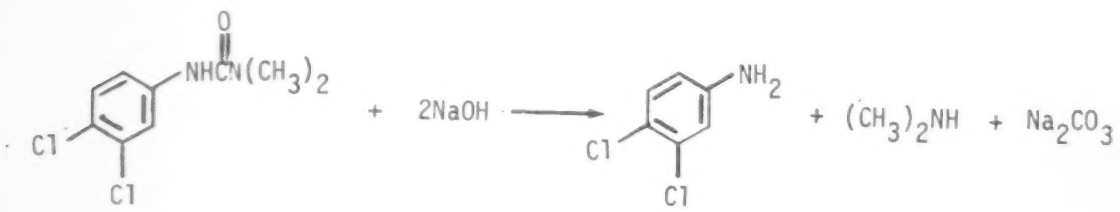
Depending on whether hydrogen sulfide or elemental sulfur is formed from the hydrolysis of captan, 3 to 4 moles of NaOH will be required to neutralize the hydrolysis products from one mole of captan. For the detoxification of 1 lb of 80 percent captan wettable powder, 1 gal of 10 percent NaOh is recommended. The amount of NaOH recommended is approximately 50 percent in excess of the stoichiometric requirement. The amount of 10 percent NaOH necessary for the detoxification of captan formulations of other concentrations can be estimated in a similar manner.

B.6 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF DIURON

Diuron (N-3,4-dichlorophenyl-N',N'-dimethylurea) is an herbicide mainly used for general weed control on non-crop areas and for selective control of weed seedlings in certain crops. The usual formulations of diuron are:[64]

- Karmax diuron weed killer - a wettable powder containing 80 percent duiron
- Karmax DL diuron weed killer - a water suspansion containing 28 percent diuron (2.8 lb diuron per gallon)
- Krovar I weed killer - a wettable powder containing 40 percent diuron and 40 percent bromacil
- Krovar II weed killer - a wettable powder containing 27 percent diuron and 53 percent bromacil

Diuron is stable toward oxidation and moisture under ordinary conditions. The rate of hydrolysis is negligible at ambient temperatures and at neutral pH, but boiling with solutions of caustic alkalies or mineral acids in water causes diuron to break down with the formation of 3,4-dichloroaniline and dimethylamine or their salts:[21]



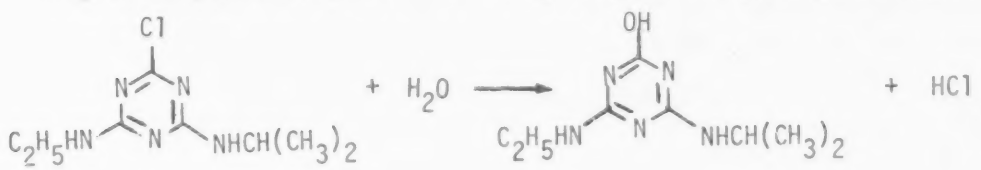
3,4-Dichloroaniline has an oral LD_{50} of 740 mg/kg for mouse and dimethylamine has an oral LD_{50} of 698 mg/kg for rats.[32] By comparison, diuron has an oral LD_{50} of 3400 mg/kg for rats. Thus the hydrolysis products of diuron have higher mammalian toxicity than the starting material and hydrolysis cannot be considered as a safe disposal method for diuron. Similarly, the other substituted ureas, such as fenuron, monuron and neburon, all result in dialkylamine and aniline or chloroaniline as hydrolysis products upon prolonged boiling with alkalies or mineral acids.[21] Chemical hydrolysis is therefore not recommended as a disposal method for the substituted urea herbicides.

Diuron is persistent in soil and may remain effective for several years as it is extremely resistant to attack by microorganisms.[25] Diuron wastes must therefore be disposed with great care to prevent unwanted sterilization of soils. For the disposal of diuron wastes, proper incineration is the only recommended procedure, although the disposal of small quantities of diuron by burial in non-crop land away from water supplies may also be considered. For the decontamination of diuron containers, the NACA triple rinse and drain procedure (Appendix D) is the only recommended method.

B.7 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF ATRAZINE

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-5-triazine) is used as a selective pre-emergence and post-emergence herbicide on many crops including maize, sorghum, sugar cane, pineapple, nursery conifers and for general weed control. The usual formulations include the 50 percent wettable powders (Gesaprim 80 and Primatol A 80).

Atrazine is stable in neutral, slightly acidic or alkaline media. In the presence of strong alkali or mineral acids, and especially at higher temperatures, atrazine is hydrolyzed to hydroxyatrazine:[21, 25, 66]



Hydroxyatrazine is herbicidally inactive and will further decompose in plants to amines and carbon dioxide.[25] Since atrazine is biologically very inactive apart from its herbicidal activity, the transformation of atrazine to hydroxyatrazine is an effective detoxification process.

Armstrong et al reported that atrazine hydrolysis followed first-order kinetics with respect to atrazine concentration at constant pH, but that the rate of hydrolysis was also both acid and base catalyzed.[66] Alkaline hydrolysis was suggested to involve direct nucleophilic displacement of the -Cl by -OH, and acid hydrolysis probably results from protonation of a ring or chain N atom followed by cleavage of the C-Cl bond by H_2O. The activation energy for the degradation reaction was reported by Zimdahl et al to be 10.8 kcal/mole.[66] However, it is not clear from the information provided whether this activation energy is applicable to acid or base catalysis. Utilizing the pH dependent rate constant relationships developed by Armstrong et al and assuming 10.8 kcal/mole as the activation energy for both acid and base catalysis (even though this is not strictly valid), the half-lives of atrazine at different pH values and temperatures have been calculated and the results of these computations are presented in Table 18. It is seen that atrazine detoxification should be conducted in strong acids or alkalies and preferably at higher temperatures.

The National Agricultural Chemicals Association indicated that acid or alkaline hydrolysis is an effective way of treating aqueous effluents from the manufacturing and formulation processes for triazine herbicides.[51] The detoxification process recommended involves adjusting of the pH of the aqueous waste to 1, followed by passing the solution through a hot water heater and then discharging into a holding pond. The concentration of the herbicide in the holding pond should be monitored to determine when it is safe to discharge the solution to the sewer. The same procedure should also be applicable to the disposal of atrazine formulations. However, since alkaline hydrolysis of atrazine is more rapid than acid hydrolysis, it is recommended that the detoxification process be carried out at pH 14. For the detoxification of 1 lb of 80 percent atrazine wettable powder, a minimum of 0.3 gal of 10 percent NaOH is recommended. This amount of

TABLE 18

EFFECTS OF pH AND TEMPERATURE ON
THE HYDROLYSIS RATE OF ATRAZINE

pH	Temperature (C)	Half-life
1	25	80 hr
1	40	33 hr
1	60	11.7 hr
1	80	4.7 hr
2	25	331 hr
3	25	1381 hr
12	25	295 hr
13	25	36 hr
14	25	4.5 hr
14	40	1.9 hr
14	60	40 min
14	80	16 min

NaOH is necessary to assure a pH 14 in the reaction solution after part of the NaOH is utilized to neutralize the HCl formed from atrazine hydrolysis. The amount of 10 percent NaOH recommended for the detoxification of atrazine formulations of other concentrations can be estimated in a similar manner. As noted previously, the alkaline treatment of atrazine is preferably carried out at higher temperatures to facilitate the rate of degradation.

The atrazine wettable powders are normally packed in bags. The empty bags should be buried in an isolated area away from water supplies.

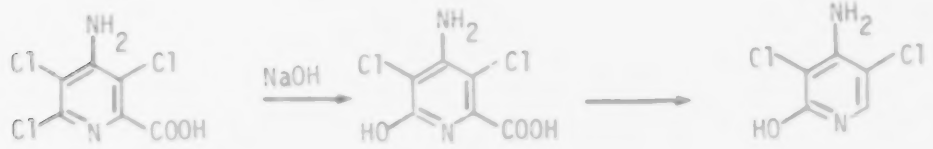
Chemical detoxification utilizing either acid or alkaline hydrolysis is also applicable to simazine and propazine. Both simazine and propazine decompose into herbicidally inactive hydroxy derivatives and their rates of hydrolysis in acid and alkaline solutions are similar to that of atrazine.[21, 25, 51]

B.8 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF PICLORAM

Picloram (Tordon, 3,5,6-trichloro-4-aminopicolinic acid) is a growth regular type herbicide used for the control of perennial and annual weeds. The amine and potassium salts of the acid are highly soluble in water and normally used in the pesticide formulations. The common formulations of picloram include:[67,68]

- Tordon 22K weed killer - a liquid containing 24.9 percent of the potassium salt of picloram (2 lb acid equivalent per gallon) and 75.1 percent isopropanol, water and dispersing agents.
- Tordon 101 Mixture weed and bush killer - a liquid containing 10.2 percent of the trisopropanolamine salt of picloram (0.54 lb acid equivalent per gallon), 39.6 percent of the trisopanolamine salt of 2,4-D (2.0 lb acid equivalent per gallon) and 50.2 percent sequestering agents, water and isopropanol.

Information on potential chemical detoxification methods for picloram is sparse. Kennedy et al reported that treatment by hydrogen peroxide (5, 15 and 30 percent), nitric acid (4N, 8N, and 16N), sulfuric acid (9N, 18N, and 36N), and ammonium hydroxide (5N, 7.5N, and 15N) had no significant effect on the potassium salt of picloram.[52] Upon treatment with sodium hydroxide (2N, 4N, and 8N), however, picloram was decarboxylated and the chlorine present was replaced by an OH group. Since 3,5-dichloro-4-amino-6-hydroxypicolinic acid has been isolated as a metabolite in wheat and the 6- position is expected to be more reactive than the 3- and 5- positions, it is probable that the initial reaction in sodium hydroxide also occurs at the 6- position:[69]



The extent of dehalogenation of piclorams in the sodium hydroxide solution was not given by Kennedy et al. The reaction products may therefore be a mixture of 3,5-dichloro-6-hydroxy-4-aminopyridine, 3-chloro-5,6-dihydroxy-4-aminopyridine, 5-chloro-3,6-dihydroxy-4-aminopyridine, and 3,5,6-trihydroxy-4-aminopyridine. The toxicity and the herbicidal activity of these products are not known at this point.

In a later study, Kennedy et al found that treatment with liquid ammonia-metallic sodium or liquid ammonia-lithium caused 100 percent degradation of picloram.[44] Again, the identity and the toxicity of the reaction products are not known. This chemical degradation process also involves the handling of hazardous and highly reactive reagents and cannot be recommended as a disposal method for picloram.

For spills or leaks involving picloram formulations, Dow recommends absorption with inert materials such as sand followed by burial of the waste in non-crop land away from water supplies.[67,68] Dow has no specific

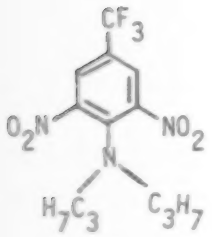
chemical procedure for the disposal of picloram.[70] For the disposal of small quantities of picloram formulations, Lawless et al recommends the precipitation of the free acid from its solution by the addition of a mineral acid, followed by incineration of the picloram acid and disposal of the dilute residual solution in an area where several years persistence in the soil can be tolerated.[1] This is probably the best disposal procedure based on present knowledge.

For the decontamination of picloram containers, the NACA triple rinse and drain procedure (Appendix D) is the only recommended method.

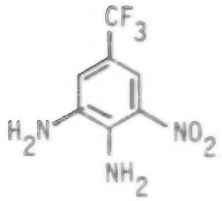
B.9 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF TRIFLURALIN

Trifluralin (Treflan, 2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline) is a pre-emergence herbicide with little post-emergence activity for the annual weeds in cotton, soybeans, and several other crops. The usual formulations include a 4 lb/gal emulsifiable concentrate (Treflan EC) and 5 percent granules (Treflan 5G).

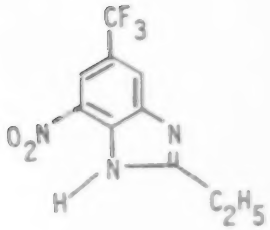
Trifluralin is resistant to oxidation and acid and alkaline hydrolysis. Kennedy et al reported that treatment by hydrogen peroxide, nitric acid, sulfuric acid, and sodium hydroxide had no significant effect on trifluralin, although ammonium hydroxide treatment did result in a color change.[52] On the other hand, trifluralin has been known to be susceptible to photochemical docomposition.[71] Crosby and Leitis reported that photodecomposition of trifluralin was rapid under acidic conditions, but above pH 7.4 the rate declined sharply and the product portions changed.[72] 2-Amino-6-nitro-4-trifluoromethylaniline (II) was found to be the principal product under acidic conditions while 2-ethyl-5-nitro-7-trifluoromethylbenzimidazole (III) was the principal product in base. A multitude of other degradation products was also detected.



Trifluralin



II



III

The major hydrolysis products of trifluralin would be identical to those formed from photodecomposition at the same pH. These degradation products are believed to be herbicidally inactive but their total environmental effects, such as the toxicity to fish, are not known at present.

Elanco Products does not recommend any chemical degradation/detoxification method for the disposal of trifluralin.[73] The major environmental effect of concern in the disposal of trifluralin is its toxicity to fish. Contamination of any body of water by disposal of wastes or cleaning of equipment should therefore be avoided. Trifluralin is known to be strongly adsorbed onto the soil and is resistant to movement by water, and burial in specially designated landfills or isolated areas away from water supplies is the procedure recommended by Elanco for the disposal of small quantities of trifluralin.[73] The best method of disposal, of course, is to use trifluralin according to label directions.

For the decontamination of trifluralin containers, the NACA triple rinse and drain procedure (Appendix D) is recommended.[73] Rinse solutions from containers can be poured into the spray tank for application. Trifluralin bags should be destroyed when empty and disposed of through regular refuse collection system or buried in an isolated area away from water supplies.[74]

APPENDIX C

CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF HALOGEN-CONTAINING PESTICIDES

C.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

A number of chemical methods are potentially applicable for the detoxification of the halogen-containing pesticides. It is well known that DDT undergoes dehydrochlorination in alkaline solutions to DDE. The use of zinc in ethanol or sodium iodide in acetone is effective in the dehalogenation of 1,2-dihalides.[75] Chau recently reported the reduction of chlordene and heptachlor with prolonged boiling in an acetone solution of chromous chloride.[76] Dennis suggested the use of nickel boride to replace the more expensive palladium on charcoal, raney nickel or cobalt as a catalyst for dehalogenation.[77] Kennedy et al showed that treatment with liquid ammonia and metallic sodium or lithium caused complete degradation of 2,4-D, DDT, dieldrin, dalapon, and 2,4,5-T.[44] Several other investigators have demonstrated that a metallic sodium-butanol, tetrahydrofuran (THF) system or lithium-butanol-THF system is equally effective in leading to total dehalogenation.[77]

The major problem with the chemical dehalogenation methods described above is that most of these methods involve the use of costly and specific chemical reagents that are often hazardous. In addition, the extent of dehalogenation, and hence the identity and environmental hazards of the degradation products are almost always unknown. At the present time, there are no practical chemical degradation/detoxification processes for the disposal of halogen-containing pesticides. Alternate disposal methods and more detailed decomposition chemistry of the specific pesticides will be discussed in the following sections.

C.2 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF METHOXYCHLOR

Methoxychlor (1,1,1-trichloro-2,2-bis [p-methoxyphenol] ethane) is used for the control of a wide variety of insects attacking fruits, vegetables, field and forage crops, and livestock, as well as certain household and industrial insects. The usual formulation is a 50 percent wettable powder (Marlate 50).

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Methoxychlor is resistant to oxidation and similar to DDT in its chemical properties. The dehydrochlorination of methoxychlor, however, takes place considerably more slowly than DDT. Melnikov reported that the rate constant of the reaction of DDT with KOH in alcohol at 40.19 C was 192 times greater than that of the p,p'-isomer of methoxychlor at the same temperature.[21] Du Pont also indicated that alkali treatment of methoxychlor is ineffective.[78] In addition, the environmental hazards of the alkaline hydrolysis degradation product, 1,1-dichloro-2,2-bis (p-methoxyphenyl) ethylene, are not well known.

Methoxychlor is susceptible to catalytic dehydrochlorination by heavy metal catalysts.[3] However, the reaction conditions and the extent of dehydrochlorination have not been investigated. The reaction product is likely to be the diphenylethylene derivative identical to that obtained from alkaline hydrolysis. Catalytic dehydrochlorination therefore cannot be recommended as a disposal method.

Du Pont recommends incineration with scrubbing as the disposal method for methoxychlor.[78] For the disposal of small quantities of methoxychlor and empty bags, burial in non-crop land away from water supplies is the only practical and recommended method.

C.3 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF CHLORDANE

Chlordane (1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene) is a broad spectrum insecticide for house and institution use. The common formulations include solutions containing 20 to 50 percent technical chlordane in deodorized kerosene and emulsifier, 25 to 40 percent wettable powders and dusts, and 5 to 3 percent granules.[79]

Technical grade chlordane contains 60 to 75 percent of the cis- and trans-isomers of chlordane, and 25 to 40 percent of related compounds, including chlordene, heptachlor and nonachlor.[21] Under the influence of caustic alkalies, chlordane undergoes partial dehydrochlorination. The cis-isomer (α-chlordane) is thought to be more readily dehydrochlorinated than the trans-isomer (β-chlordane), but the splitting out of more than

two chlorine atoms is not possible even for α-chlordane under ordinary conditions.[20] Bowery indicated that chlordane was dechlorinated by alkali to yield nontoxic products.[24] This statement was not verified by Velsicol.

Sweeny and Fischer demonstrated that chlordane could be substantially degraded by the mildly acidic reduction of zinc powder or zinc-copper couple.[80] Melnikov also reported that more than two chlorine atoms were split out when chlordane was acted on by zinc dust in acid medium.[21] However, the degradation products were not identified and the zinc ions formed are toxic and pose another environmental problem. Zinc reduction is therefore not considered as an acceptable disposal method for chlordane.

In the analysis of chlordane formulations, the total chlorine content is determined by converting all organically bound chlorine to chloride ion by using a metallic sodium-isopropyl alcohol solution and refluxing vigorously for 30 minutes.[24] This again is not a practical disposal method.

Velsicol indicates that no practical chemical treatment is available for chlordane at this time.[79] The basic objection to the use of alkali treatment is that several days to weeks contact time may be required to insure complete hydrolysis. For the disposal of excess chlordane, Velsicol recommends incineration at 1800 to 2000 F, with a residence time of a minimum of one second. This is in agreement with the recommended incineration conditions from a recent TRW study on the thermal degradation of chlorinated hydrocarbon pesticides.[81] For the decontamination of chlordane containers, the triple rinse and drain procedure developed by NACA (Appendix D) is recommended. If correctly followed, the rinsed containers can be safely handled for disposal, recycling for metal, or drum reconditioning.

C.4 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF TOXAPHENE

Toxaphene is a complex mixture of polychlorinated camphenes containing 67 to 69 percent chlorine and has the approximate composition of $C_{10}H_{10}Cl_8$. It is a non-systemic and persistent contact and stomach insecticide. Toxaphene is marketed as a 90 percent toxaphene - 10 percent solvent

solution using mixed or modified xylene as the solvent.[82] This solution is then formulated by various companies into emulsifiable concentrates, either alone or with other insecticides. Little or no toxaphene is currently being used in dust, wettable powder, or granule formulations.

Treatment by alkalies causes toxaphene to split out part of the chlorine but does not lead to complete degradation.[21] In laboratory experiments conducted at Tenneco Chemicals, the dehydrochlorination of toxaphene by refluxing one part with 100 parts of 2 percent alcoholic potassium hydroxide removed 33 percent of the total chlorine in one half hour.[83] The same reagent at room temperature removed 25 percent of the chlorine in five hours. Tenneco indicated that there was evidence that the dehydrochlorinated residue was less active biologically and less toxic but the reaction product mixture has not been further characterized. In a recent Russian study by Lyubenko et al, it was found that boiling toxaphene for six hours in water resulted in 98 percent degradation of toxaphene, but the extent of dehydrochlorination was not specified and may be minor.[83]

In the analytical determination of toxaphene, several methods are available for converting all organically bound chlorine to chloride ion. These decomposition procedures include the reaction of toxaphene with metallic sodium in isopropyl or isobutyl alcohol, metal-organic reagents such as sodium biphenyl, and metallic sodium in liquid ammonia.[24] None of these can be considered as practical disposal methods.

For the disposal of small quantities of toxaphene, both Hercules and Tenneco recommend either fuel assisted incineration or burial in a secure landfill lined with an impervious material or naturally isolated from groundwater.[82,83] Alkali treatment is the chemical method that offers the best possibilities but cannot be recommended because it does not lead to complete detoxification.

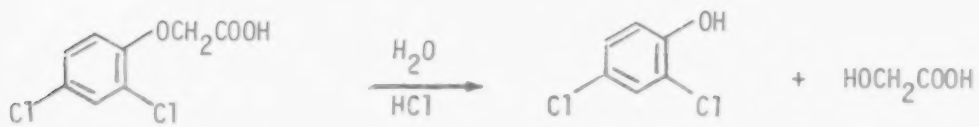
A significant portion of the 90 percent toxaphene is delivered in 55 gallon lined drums. For the decontamination of these containers, the

drums should be drained as completely as possible and then carefully rinsed with repeated rotation. A triple rinse with about a gallon of solvent (xylene or the safer mineral spirits, if compatible with the formulation) is recommended by Tenneco.[83] The rinse solution can be added to the next formulation batch and the drum can be sent to a drum reconditioner for restricted reuse. For the decontamination of containers for toxaphene emulsifiable concentrates, the NACA triple rinse and drain procedure (Appendix D) is recommended. The rinse solution can either be added to the spray tank or buried in non-crop lands away from all possible contact with water supplies. The containers should either be sent to a drum reconditioner or made useless by punching holes in them followed by burial in landfill operations.

C.5 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF 2,4-D

2,4-D (2,4-dichlorophenoxyacetic acid) and its salts and esters are systemic herbicides widely used for the weeding of cereals and other crops. 2,4-D is not normally used in the free acid or sodium salt form because of low solubility and limited herbicidal activity. The most common forms of 2,4-D are the dimethylamine, ethanolamine, and mixed alkanolamine salts and isopropyl, butyl, iso-octyl and propylene glycol butyl ether esters. The amine salts are usually marketed as solutions of declared 2,4-D content (e.g., Dow DMA-4 herbicide). The esters are usually formulated as emulsifiable concentrates (e.g., Esteron 99 Concentrate weed killer).

The free acid form of 2,4-D reacts with inorganic bases to form stable salts and is resistant to further reaction. On prolonged boiling with HBr or HCl, 2,4-D decomposes to 2,4-dichlorophenol and glycollic acid:[21]

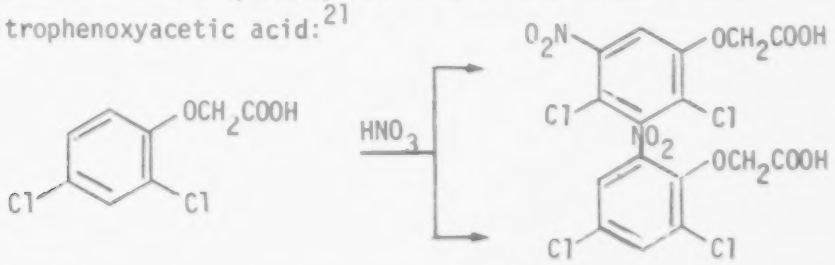


2,4-Dichlorophenol is also obtained by the chemical cleavage of the ether bond when 2,4-D is fused with pyridine hydrochloride.[84] 2,4-Dichlorophenol

is an intermediate soil degradation product of 2,4-D and is extremely susceptible to photodecomposition.[85,86,87] However, neither method described above for converting 2,4-D to the phenol is suitable as a general disposal technique.

The NACA Waste Disposal Manual reported that chlorination of liquid 2,4-D waste by adding sodium hypochlorite solution or gaseous chlorine at pH 3 and temperatures above 85 F for at least 10 minutes would render the phenoxys nonherbicidal.[51] The chlorination products were not identified. According to Melnikov, the chlorination of 2,4-D with gaseous chlorine yields 2,4,6-trichlorophenoxyacetic acid, but at 200 to 205 C, disintegration products are also found, including 2,4-dichlorophenol, bis (2,4-dichlorophenoxy) methane, and others.[21] When the ethyl ester of 2,4-D is chlorinated at 195 to 210 C, the esters of 2,4-dichlorophenoxy-chloro- and dichloroacetic acids and 2,4-dichlorophenyl chloromethyl ether are obtained.[21] Some of the same products are probably also obtained in the chlorination of 2,4-D at pH 3. The environmental effects of these products are not completely known. Chlorination therefore cannot be recommended as a disposal method for 2,4-D at the present time.

Kennedy et al reported that hydrogen peroxide (5, 10 and 30 percent) had no significant effect on 2,4-D.[52] Melnikov indicated that the main product of the nitration of 2,4-D by nitric acid or nitrating mixture is 2,4-dichloro-5-nitrophenoxyacetic acid with a small trace of 2,4-dichloro-6-nitrophenoxyacetic acid:[21]



The toxicity and the environmental hazards of the nitration products are unknown. Both nitration products may be herbicidally active. Nitration is therefore not an acceptable disposal method.

The use of metallic sodium or lithium in liquid ammonia to cause 100 percent degradation of 2,4-D has also been reported.[44] The degradation products were not identified. This again is not a practical disposal method.

In summary, there are no practical chemical degradation/detoxification methods for 2,4-D disposal. 2,4-D is known to be readily detoxified by soil microorganisms and at low dosages is normally decomposed in one to four weeks.[25] The detection of 2,4-dichlorophenol, 4-chlorocatechol, chloromuconic and succinic acids from either soil or pure culture studies suggests a sequence of reactions involving ring hydroxylation and cleavage and further metabolism of the open chain structure to carbon dioxide.[85,86,88] The non-persistence and detoxification of 2,4-D in soil indicate that burial in non-crop areas away from water supplies would be an acceptable method for the disposal of small quantities of 2,4-D.

Strong solutions of acid, amine or other salts of 2,4-D can be precipitated with calcium or magnesium salts to reduce the quantity of herbicides requiring disposal and minimizing the potential for water contamination as a result of leaching.[51] This technique is not applicable to the 2,4-D esters.

Dow recommends incineration in a high temperature incinerator to dispose of small amounts of unused 2,4-D.[70] The recent TRW study recommends incineration at temperatures above 1660 F for at least 0.3 seconds for the complete degradation of 2,4-D esters.[81] Incineration at high temperatures with sufficient residence time leads to complete detoxification of 2,4-D and is the most environmentally acceptable method for 2,4-D disposal.

For the decontamination of 2,4-D containers, the NACA triple rinse and drain procedure (Appendix D) is recommended. The small containers should be punched full of holes, crushed and taken to a landfill. Large containers (30 and 55 gallon drums) can be sent to a drum reclaimer or a scrap metal dealer after rinsing according to the NACA procedure.

C.6 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF AMIBEN

Amiben (chloramben, 3-amino-2,5-dichlorobenzoic acid) is a selective pre-emergence herbicide suggested for use on soybean, carrots and cucurbitaceous crops, and also on transplanted crops. The common formulations include an aqueous solution of the ammonium salt containing 2 lb acid equivalent/gallon (Amiben), a granule containing 10 percent acid equivalent as the ammonium salt (Amiben Granular 10 percent), and 4 and 1.2 percent granules as ornamental and garden weed killers.

Amiben is stable to heat, to oxidation, and to hydrolysis by acid or alkaline media.[3, 20] Treatment by sodium hypochlorite rapidly decomposes amiben. The chemistry of decomposition is unknown but probably involves the generation of both mono- and dichloroamino compounds as the principal products. The identity of these degradation products has not been confirmed and the environmental effects are completely unknown. The use of sodium hypochlorite as a chemical reagent to detoxify amiben is considered to be unacceptable by Amchem Products.[89]

As described in C.1, several chemical reducing agents, such as the use of a combination of hydrazine and palladium charcoal, are effective in dehalogenating the haloaromatic compounds.[90] However, none of these reagents can be considered in any practical disposal method.

Amiben is readily susceptible to photolysis by visible light. For example, sunlight or a fluorescent sunlamp caused an aqueous solution to become colored, probably as a result of polymerization process.[69] Illumination by a lamp with a borosilicate glass filter has been reported to cause rapid dechlorination at the 2-position.[69] The reaction products from the photodecomposition of amiben have not been completely characterized and it is questionable whether photolysis can be considered as a practical method for the disposal of small quantities of pesticides.

In summary, the use of chemical reagents as a means of amiben disposal is not recommended at the present time. Amchem Products indicates that amiben's shelf life is of sufficient duration to allow for total use of

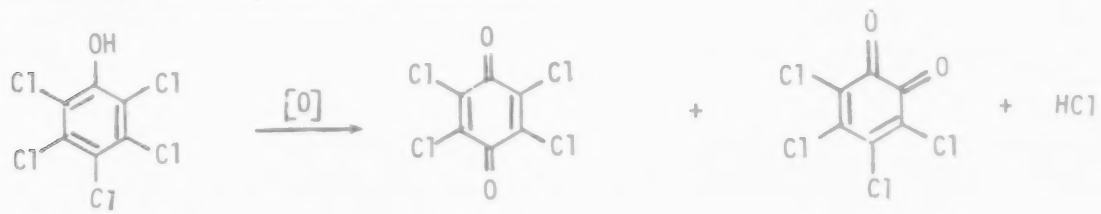
the product in accordance with label directions.[89] On this basis, there should be few instances of small quantities of excess amiben requiring disposal.

For the decontamination of amiben containers, the NACA triple rinse and drain procedure (Appendix D) is again recommended. The rinse solution can either be added to the spray tank or buried in non-crop lands away from water supplies.

C.7 CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF PENTACHLOROPHENOL

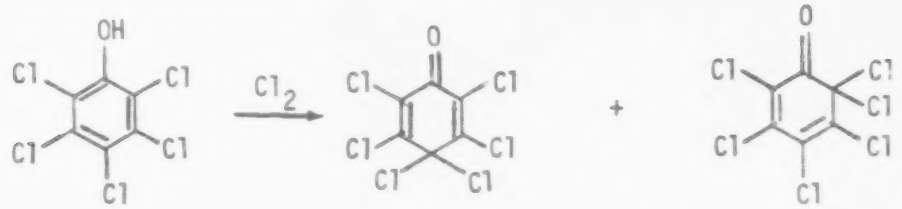
Pentachlorophenol (PCP) is an insecticide used for termite control and the protection of cut timber from wood-boring insects and from fungal rots. It is also strongly phytotoxic and hence used as a pre-harvest defoliant and as a general herbicide. Pentachlorophenol is marketed in the form of technical grade crystals, solution concentrates (e.g., Dowicide 7, penchlorol, penta) or as sodium pentachlorophenate granules (Dowicide G, Santaborite, Weedbeads). The technical grade crystals or solution concentrates are designed for use by large consumers for wood preservation. The normal procedure is to dissolve or dilute pentachlorophenol to a 5 to 7 percent solution with petroleum solvents and impregnate the wood by pressure treatment.[91]

Pentachlorophenol is decomposed by most, but not all, strong oxidizing agents. For example, with nitric acid, tetrachloro-p-quinone (chloranil) and tetrachloro-o-quinone are obtained:[21]



Chloranil is a disinfectant that is stable to acids but reacts with alkalies to form salts of chloranilic acid.[20] Thus chemical oxidation of pentachlorophenol does not lead to complete detoxification.

The chlorination of pentachlorophenol gives derivatives of cyclohexene known as hexachlorophenols:[21]



The hexachlorophenols are fungicidal and have been proposed for seed disinfection. Chlorination is therefore not an acceptable disposal method.

Sodium pentachlorophenate is highly soluble in water and can be converted to pentachlorophenol by the addition of a strong mineral acid. The pentachlorophenol is practically insoluble in water and therefore minimizes the potential for water contamination when buried in ground. There are no practical chemical methods for pentachlorophenol detoxification. The only method recommended for the disposal of small quantities of pentachlorophenol is to bury the material in an approved and designated landfill or in an isolated area away from water supplies.[91]

The containers for the technical grade crystals and sodium pentachlorophenate are paper bags. These should be emptied as thoroughly as possible and then buried in an approved and designated landfill or an isolated area away from water supplies. The solution concentrates are usually delivered in metal cans or drums. These should be rinsed three times with fresh portions of the diluting solvent which is then added to the dilute mixture for wood impregnation.

APPENDIX D
NACA TRIPLE RINSE AND DRAIN PROCEDURE

The National Agricultural Chemicals Association (NACA) recommends the following decontamination procedure for pesticide containers:

1. Empty container into spray tank. Then drain in vertical position for 30 seconds.
2. Add a measured amount of rinse water (or the designated spray carrier) so container is 1/4 to 1/5 full. For container size less than 1 gallon, add an amount of rinse solution equal to 1/4 of the container volume. For a 1 gallon container, add 1 quart of rinse solution. For a 5 gallon container, add 1 gallon of rinse solution. For 30 and 55 gallon containers, add 5 gallons of rinse solution.
3. Replace closure. Shake container or roll and tumble to get rinse on all interior surfaces. Drain rinse solution into sprayer or mix tank. Continue draining for 30 seconds after drops start.
4. Repeat the above steps for total of 3 rinses. 1 gallon and 5 gallon steel containers should be punctured before draining the 3rd rinse. It is recommended that the container be punctured in the top near the front sprout to allow for complete drainage of the third rinse.
5. For 30 and 55 gallon steel containers, replace closures and secure tightly and send the containers to an approved drum reconditioner (check with State Department of Agriculture for list) or recycle as scrap into a steel melting plant. For 1 gallon and 5 gallon steel containers, crush immediately and recycle for scrap to a steel melting plant. For glass containers, break or crush into large container (such as 55 gallon open headed drum with cover) and recycle for scrap to a glass melting plant. If the above preferred container disposal method cannot be accomplished, the container should be crushed and buried at an approved dump site. Do not reuse containers.

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